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Synthetic and natural muscovites

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(*Received* 30 *June* 1955)

ABSTRACT

The syntheses of randomly stacked one-layer monoclinic (1Md), one-layer monoclinic (1M), and two-layer monoclinic (2M) muscovite, have been accomplished. The upper stability limit of muscovite is represented by a curve passing through the points 625°C, 5000 p.s.i. water pressure; 665°C, 15,000 p.s.i.; and 715°C, 30,000 p.s.i. Immediately above this curve sanidine + corundum + vapour are the stable phases.

The stability ranges of the muscovite polymorphs named could not be fixed accurately because of the sluggish nature of the transformations; however, the transformation of 1Md → 1M → 2M was effected. It is believed that this sequence obtains in the progressive metamorphism of a sediment. The first transformation is probably dependent on factors affecting reaction rate. The second transformation may be related to a univariant curve of equilibrium (i.e., an isograd). The growth of a three-layer trigonal muscovite (3T) was suspected in only one run with 2M muscovite, and its synthesis is, therefore, not substantiated.

Study of natural muscovites and muscovite-like materials indicates that the hitherto unrecognized 1Md and 1M muscovites are common. Their relation to materials called illite, high-silica sericite, hydromuscovite, as well as other dioctahedral minerals, is described.

The complete destruction of the muscovite structure by grinding is demonstrated by selected area electron diffraction studies. The alleged resynthesis of muscovite by further grinding is shown to be suspect.

A comparison of the maximum upper stability curve of muscovite with the minimum melting curve of the "granite" system suggests that muscovite may form in granitic magmas above approximately 1500 atmospheres water pressure, and in the solid state below that pressure in granitic rocks when the water pressure equals the total pressure. These relations may account for the apparent two generations of muscovite in some granites. A limitation on the amount of muscovite in igneous granites is believed to be imposed by the character of the liquidus surfaces.

The upper stability curve of muscovite marks the maximum possible conditions of the second sillimanite or orthoclase isograd in metamorphic rocks.

The nature of the processes of weathering, abrasion, and diagenesis of muscovite in sediments is outlined.

Introduction

Muscovite is the most common of the micas and occurs over a large range of geological conditions. It is a principal constituent of the fine-grained sediments, many of the metamorphic rocks, and some classes of salic igneous rocks. The occurrence of muscovite is, however, limited in certain respects. Muscovite is believed by some to weather to clay minerals. Muscovite breaks down at the highest grade of metamorphism and is absent in those igneous rocks thought to have formed at the higher temperatures; that is, it is not common in hypabyssal salic igneous rocks, and is absent in extrusive rocks. In addition, the high alumina content of muscovite imposes further restrictions on its occurrence. The occurrences and absence of muscovite raise many questions concerning its stability, and it is the purpose of this investigation to seek an understanding of these limitations of formation.

This is the second paper on a series of studies of the mica group. The results of the investigation of the stability range of phlogopite appeared in 1954, and the results of experiments on paragonite will follow.

Natural Muscovites

There are two ordered polymorphs of muscovite, two-layer monoclinic (2M) and three-layer trigonal (3T), known from the studies of Jackson and West (1931, 1933), Hendricks and Jefferson (1939), Axelrod and Grimaldi (1949), and Smith and Yoder (1955). All twenty muscovites examined by Hendricks and Jefferson had a 2M structure. Of the 150 muscovites examined by Heinrich *et al.* (1953), three which were high in silica had a 3T structure, and the rest 2M. The six muscovites examined by Smith and Yoder had 2M structures with the exception of one 3T structure which had been previously described by Axelrod and Grimaldi (1949) as a three-layer monoclinic structure. The existence of a one-layer, monoclinic (1M) structure in synthetic muscovite briefly referred to by Yoder and Eugster (1953) is demonstrated, and some of the occurrences of such micas in nature are listed below.

The theoretical polymorphs, two-layer orthorhombic (2O) and the six-layer hexagonal (6H), predicted by Smith and Yoder (1955), have not been observed. Of the more complex muscovite polymorphs, 8-, 12-, and 18-layer structures are known. The 18-layer specimen has been observed by the multiple beam interferometry method, and is believed by Amelinckx and Dekeyser (1953) to be due to spiral growth.

In addition to the ordered polymorphs of mica, there exists a disordered one-layer, monoclinic polymorph (1Md), which is described in detail in a following section.

The muscovites are known also in mixed-layer structures, particularly the 1M in association with montmorillonite. The theory of the X-ray diffraction phenomena for the mixed-layer structures has been worked out by Hendricks and Teller (1942) and extended by Brown and MacEwan (Brindley, 1951). Such structures are important in some classes of minerals, and have not been fully recognized. In the ensuing arguments concerning the problems of the illites, hydromicas, and sericites, it is necessary to describe the various types of mixed-layer structures. For this reason a brief synopsis of the powder X-ray diffraction phenomena is presented, so that the mixed-layer types may be readily identified. In Fig. 1 are given schematically portions of the X-ray pattern in the critical low-angle region which distinguishes the various mixed-layer types. Fig. 1a is the 001 peak of a 1M muscovite, and in Fig. 1c is the 001 peak of a montmorillonite having one layer of water. If equal portions of 1M muscovite and montmorillonite are mixed together mechanically, the resulting X-ray powder pattern will be as in Fig. 1d. A similar pattern would obtain if montmorillonite and 1M muscovite had grown as individual crystals in a rock. The peak heights would vary, of course, in proportion to the amount of each phase present. If montmorillonite and 1M muscovite are intergrown in such a manner that they are interstratified in random fashion, the X-ray powder pattern is as in Fig. 1b. The single sharp peak represents the *apparent* spacing of the randomly interstratified phases, and its position between the 001 peaks of the end members is a measure of the proportions of the two phases. In the case of the 001 peaks of montmorillonite and 1M muscovite the proportionality is essentially linear (see Brown and MacEwan in Brindley, 1951, p. 277, for the precise relation). It is also possible that montmorillonite and 1M muscovite are interstratified

in a regular fashion such as *ABABAB*, in which case the powder pattern is as in Fig. 1e. For such regular interstratification the repeat unit is now the sum of the two end-member cells and, therefore, subsidiary reflections may be observed having spacings which are submultiples of 22·4 Å. This would occur if the ratio of montmorillonite to 1M muscovite was 1 : 1. The intensity of the subsidiary reflections would depend upon the perfection of the repeat. The

Fig. 1. Schematic X-ray powder patterns in the low-angle region:
(*a*) 1M muscovite, 001 reflection
(*b*) random mixed-layer 1M muscovite and montmorillonite
(*c*) montmorillonite (one-layer of water)
(*d*) mechanical mixture of 1M muscovite and montmorillonite, 1 : 1
(*e*) regular mixed-layer 1M muscovite and montmorillonite, 1 : 1
(*f*) predominantly muscovite with a continuum of randomly interstratified montmorillonite crystallites.

intensities in Fig. 1e were chosen to represent those of a natural example described by Heystek (1954, p. 404). Other ratios of *A* to *B* are possible, and the subsidiary reflections will occur in submultiples of the new combined cell. It may not be possible to distinguish very large combined cells from random interstratification because of the high background in the low-angle region. Other types of more complex mixed-layer structures have been observed. For example, in Fig. 1f a portion of a powder pattern is given for a sample in which the larger portion is of 1M muscovite, yet there is a continuum of crystallites of randomly interstratified mica and montmorillonite in decreasing proportions from mica to montmorillonite. Examples of mixed-layer structures are presented below.

Previous Experimental Studies

Synthesis

Previous syntheses of muscovite were accomplished, using a variety of techniques—reaction of phases of appropriate composition, recrystallization of decomposed natural mica, or the alteration of natural minerals or glasses. The first synthesis of hydroxyl-bearing muscovite from the appropriate components was achieved by Noll (1932). He produced a mica from a gel close to the requisite composition at 225–300°C and 26–90 atm in runs of about five days' duration. The X-ray spacings for one product are given in Table 6 for reference. Using $Al(OH)_3$, "silicic acid," and KCl in HCl solutions at 400°C, 350 atm, for five days, J. W. Gruner (1939, 1944) obtained an X-ray pattern of muscovite from the product (J. W. Gruner, 1942, p. 132). The interplanar spacings of his synthetic mica are also given in Table 6. Bowen and Tuttle (unpublished, 1952) identified muscovite on the surface of some of their charges after hydrothermally crystallizing glasses near the anhydrous muscovite composition in the system K_2O—Al_2O_3—SiO_2. Kiyoura and Ito (1953) also appear to have been successful in synthesizing muscovite from the requisite components. Their initial materials were KOH + $Al(OH)_3$ + SiO_2 gel in the proper ratio. These were held at 340–350°C at about 150 atm for eleven days. The X-ray and differential thermal analysis patterns, although subject to question, support their conclusion. The intensities of the X-ray pattern are not in accord with those of Noll, but the interplanar spacings are close.

The resynthesis of muscovite from its decomposition products is reported by E. Gruner (1929) and Roy (1949). E. Gruner treated natural muscovite with 0·5N KOH at 400°C in a bomb, and obtained "kaliophilite" on which muscovite appears to have grown. Roy decomposed a muscovite by heating at 1050°C, after which treatment only γ-Al_2O_3 (or spinel?) was identified. This product was held at 400–650°C and 1000–10,000 p.s.i. water pressure for 12–100 hours. The X-ray pattern of the final product was believed to be that of a mica with broadened peaks.

Synthesis by the alteration of other minerals containing some of the necessary components has also been found fruitful by several workers. As early as 1894 Thugutt heated "kaliophilite" with H_2O at about 200°C, and obtained a micaceous product. The partial alteration of nepheline, orthoclase, and leucite to "sericite," using CO_2-charged percolating water at 250–350°C, 250–500 p.s.i., for 320 hours on the average, was accomplished by Norton (1939). J. W. Gruner (1944) and O'Neill (1948) were successful with similar experiments, using natural microcline and albite. These minerals were altered with HCl solutions containing KCl and $Al(OH)_3$ at 300–525°C, 250–300 atm, for 7–17 days. Gillingham (1948, p. 257) held bayerite and microcline in separate crucibles in a bomb at 575°C and 440 kg/cm^2 for 31 days. Potash and silica leached from the microcline were transported in the vapour and reacted with the bayerite to form muscovite and an unidentified isotropic material. Montmorillonite can be transformed into a mica, according to Caillère and Hénin (1949), by treatment with a 1N KCl solution and then boiling in a 1N KOH solution. The principal X-ray spacing was 10·2 Å, and the product did not expand in glycerol. Morey (1955, unpublished) passed 194 litres of H_2O over a microcline from Buckingham, Quebec, at 350°C and 5000 psi during a period of 103 days. The surfaces of the feldspar fragments were found by the present writers to be covered with 1M muscovite and boehmite. The mica crystals were approximately 30 to 50 μ on the longest dimension. The solution contained a 10 per cent excess of $K_2O \cdot 6SiO_2$ over the ratios $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ required for the feldspar. In another experiment, Morey passed 78 litres of H_2O over an albite from Amelia Co., Va., which contained 0·20 per cent K_2O at 350°C and 5000 p.s.i. during a period of thirty-eight days. The surface of the albite was coated mostly with 1M muscovite and a small amount of paragonite, analcite, and boehmite.

The synthesis of muscovite has also been reported from more complex systems for which the composition of the final products has not been determined.

Decomposition

The muscovite structure breaks down when the mineral is heated in air at elevated temperatures. Maegdefrau and Hofmann (1938a) noted that an illite[1] retained its structure with loss

[1] As is shown below, illites are polymorphs of muscovite, solid solutions close to muscovite, or mixed-layer structures.

of OH up to 1000°C, and GRIM and BRADLEY (1940) found that 850°C was required to destroy the structure of their illite. Optical changes observed by RINNE (1924) after heating muscovite at 1000°C, could be reversed by passing hydrogen over the sample. According to ROY (1949), muscovite shows no significant structural change until heated to 940°C. The loss of water is accompanied by a marked structural expansion in the *c* direction (VACHER in HIDNERT and DICKSON, 1945) which is believed to be due to the buckling of the structural layers. The loss of water only involves the loss of one-sixth of the oxygens in the octahedral layer in addition to all the hydrogens. The explanation of the persistence of the structure on loss of water proposed by GRIM and BRADLEY (1940) involves the loss of hexagonal symmetry, and therefore does not appear to be a likely solution.

On firing of muscovite at 1050°C, ZWETSCH (1934) reports that γ-Al_2O_3, α-Al_2O_3, and leucite are the products, and at 1300°C only leucite and α-Al_2O_3 are observed. GRIM and BRADLEY (1940) found that spinel appeared in illite at a temperature of about 850°C, mullite formed at 1100°C, and by 1300°C the spinel had been resorbed in liquid. Mullite persisted to at least 1400°C. ROY (1949) found that muscovite develops γ-Al_2O_3 or spinel when fired at 1000°C, α-Al_2O_3 at 1100°C, and α-Al_2O_3 + liquid above 1400°C. According to RAO, MURTHY, and SINGH (1953), muscovite heated at 1400°C yields "kaliophilite" + mullite + isotropic phase having $n = 1{\cdot}736$ + liquid. The appearance of spinel in the products observed by GRIM and BRADLEY, and possibly identified by ROY and by RAO, MURTHY, and SINGH, suggests that their original samples contained appreciable amounts of magnesia. SUNDIUS and BYSTRÖM (1953) decomposed muscovite at a series of temperatures:

1000° mullite + γ-Al_2O_3 + α-Al_2O_3 + liquid

1100° mullite + α-Al_2O_3 + liquid

1200° mullite + α-Al_2O_3 + unidentified phase [leucite?] + liquid

1260° mullite + α-Al_2O_3 + liquid.

They related the decomposition to the K_2O—Al_2O_3—SiO_2 diagram of SCHAIRER and BOWEN (1947), but did not clearly interpret the initial melting relations. From the studies of SCHAIRER and BOWEN (1955) the anhydrous muscovite composition should crystallize in the solid state to 38·26 per cent leucite + 24·40 per cent potash feldspar + 37·34 per cent mullite by weight below 1140° ± 20°C, the temperature of the ternary invariant point N of Fig. 2. At that temperature liquid appears, and increases in amount until the feldspar is consumed. Then mullite + leucite + liquid are the stable phases, and the composition of the liquid follows the boundary curve NA' (Fig. 2) to A', 1315° ± 10°C. At this temperature corundum appears by reaction of mullite and liquid. When the mullite is consumed, the stable phases are leucite + corundum + liquid. The composition of the liquid changes along the boundary curve $A'B'$ between the fields of leucite and corundum, until a point on this curve is reached which lies on the projection of a line connecting the anhydrous composition of muscovite with corundum. At this point all the leucite has been consumed by reaction, and the stable phases are corundum + liquid. Complete melting would be achieved near 1700°C. It is clear that the observed decomposition products of natural muscovite do not represent equilibrium assemblages. As will be seen below, different assemblages are stable when the decomposition of natural muscovite occurs in the presence of water under equilibrium conditions.

The muscovite structure may also be broken down by grinding at room temperature. MACKENZIE and MILNE (1953) believe that the structure is completely destroyed in about eight to nine hours of grinding in an agate mortar, and that recrystallization then takes place with the growth of hydrous mica (illite). They base their conclusions on cation-exchange capacity, X-ray powder patterns, differential thermal analysis, and chemical analysis. There are objections to the interpretation of each phase of their study with regard to the alleged recrystallization. As will be seen from the date given in the section on *Effects of Grinding*, there is no doubt that the muscovite structure can be destroyed by grinding; there is, however, considerable doubt that further grinding will bring about the synthesis of hydrous mica or illite.

Method of Investigation

Those initial materials subjected to various conditions of pressure and temperature, the apparatus used to fix the pressure and temperature, and the methods required to identify the products, are described in the following sections.

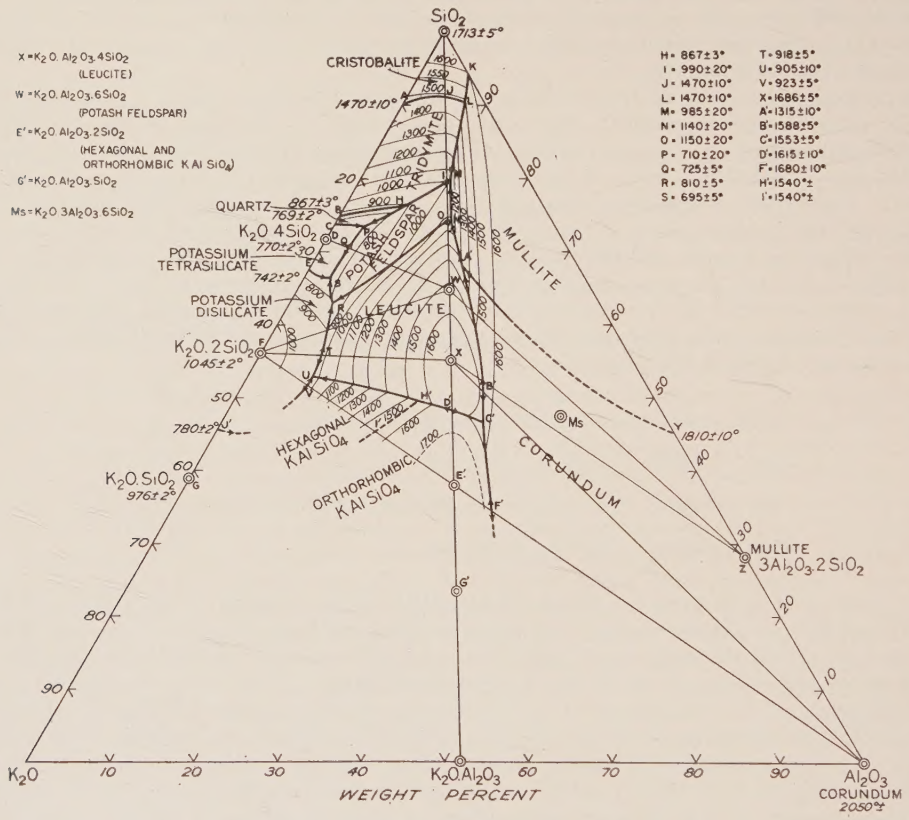


Fig. 2. Phase diagram of the K_2O—Al_2O_3—SiO_2 system (Schairer and Bowen, 1955).

Initial Materials

Experience has shown that it is often necessary to investigate a large number of materials of the requisite composition in order to establish the equilibrium products. The selection of these materials may be made from a study of a plot of all the known natural and synthetic hydrous or anhydrous materials whose composition lies in the K_2O—Al_2O_3—SiO_2—H_2O system (Fig. 3). The classic approach to synthesis is to start, when possible, with a glass of the composition of the mineral to be produced. Synthesis of hydrous minerals by subjecting glasses to a hydrothermal environment has proved to be difficult; metastable phases are readily produced and growth rates are slow. The hydrothermal reaction of the fundamental oxides has yielded satisfactory results in numerous cases; such an approach, however, is not convenient for a potash-bearing system. Considerable success has been obtained using pure natural hydrated compounds of alumina and silica, such as kaolinite, montmorillonite and pyrophyllite, mixed with the remaining necessary constituents. Another method of synthesis employs the natural mineral to be

synthesized after it has been decomposed by heating, grinding or chemical treatment. Still another method makes use of natural and synthetic anhydrous compounds which serve as end members to hypothetical joins passing through the composition of the desired mineral. In all synthesis studies it is necessary to verify the results of these and other methods by recrystallizing and decomposing the natural mineral in the regions of stability and instability, respectively. The following materials were used in the attempts to synthesize the muscovites and to determine their stability range.

(a) A mixture of synthetic $K_2O \cdot 6SiO_2$ glass prepared by J. F. Schairer, and γ-Al_2O_3 prepared in the way suggested by J. W. Greig (Yoder, 1952, p. 572), in the requisite proportions, was ground for one hour in acetone in a motor-driven, agate mortar. This mix constituted one of the initial charges subjected to hydrothermal treatment.

(b) The necessary proportions of synthetic orthorhombic $KAlSiO_4$, prepared many years ago by E. T. Allen, and an analyzed natural kaolinite, a National Bureau of Standards (1928)

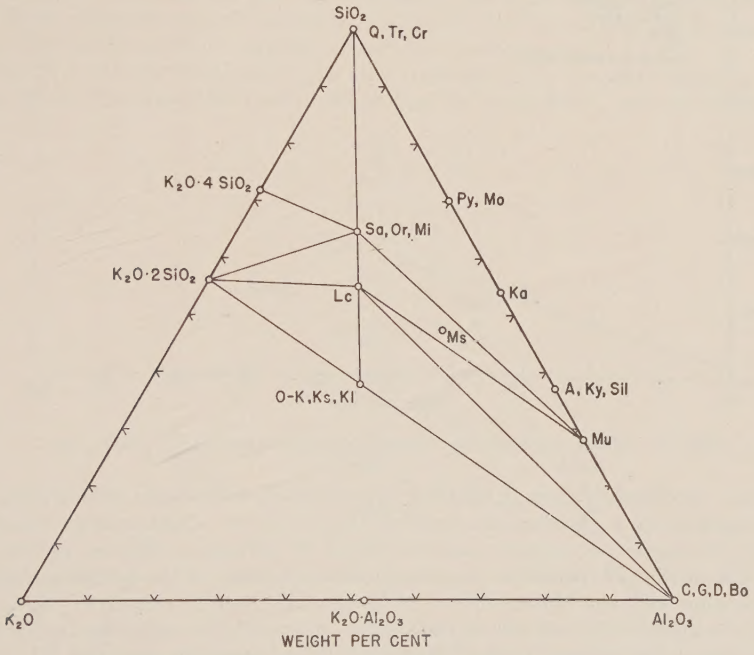


Fig. 3. One-point projection of the system K_2O—Al_2O_3—SiO_2—H_2O, showing the position of muscovite and possible initial reactants. The abbreviations are defined in Table 1. The tie lines are those of Schairer and Bowen (1955).

standard sample from Zettlitz, Czechoslovakia (see Ross and Kerr, 1931, p. 164), were ground in acetone for one hour.

(c) Several batches of glass of the anhydrous muscovite composition were made. The initial mixture in one case was γ-alumina + $K_2O \cdot 6SiO_2$ glass in the requisite proportions. A mixture of $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ (potash feldspar) glass + γ-alumina was also used as starting material. A third glass was made from a natural muscovite from Spruce Pine, N.C. (U.S.N.M. 96460). All were fired at approximately 2000°C for thirty seconds in a graphite-resistor, vacuum furnace (Urry and Piggot, 1941). The following indices of refraction of the glasses were obtained for the respective preparations: 1·532, 1·531, and 1·529. The average index of refraction of the two glasses made from synthetic materials is about 1·532 ± 0·003.

It was of interest to check the index of refraction of the glass prepared with that predicted from glasses near the anhydrous muscovite composition. A large number of glasses had been

prepared by Schairer and Bowen (1955) in their study of a portion of the K_2O—Al_2O_3—SiO_2 system. Unfortunately, their detailed study extended to only several per cent Al_2O_3 beyond the SiO_2—$K_2O \cdot Al_2O_3$ join where the melting temperatures exceed 1600°C. Furthermore, no systematic study of the glasses on the SiO_2—Al_2O_3 join appears to have been made. A compilation of the few known data on glasses on the Al_2O_3—SiO_2 join is given in Fig. 4. Only the point by Sosman (1927) and the two points by Merwin and Morey (Morey, 1954) were determined on glasses produced by the quenching method. The glasses of Kraner (1924) were made in an oxy-gas torch from mixtures of "corundum + flint." The index of refraction of the Al_2O_3 glass published by Kraner is not considered reliable, because other workers using more refined techniques have not been able to quench a liquid of that composition completely to a glass. The high index of refraction obtained by Kraner is attributed to crystallites in glass. Those

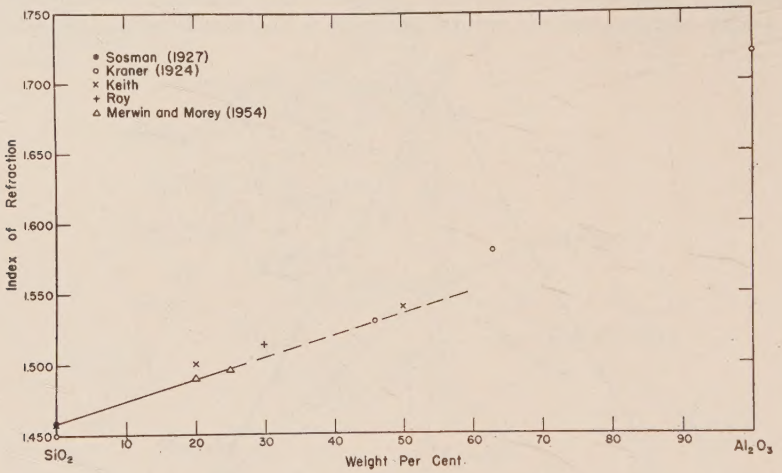


Fig. 4. Index of refraction of some glasses on the Al_2O_3—SiO_2 join.

of Keith (1954, unpublished) and Roy (1954, unpublished) were made from mixtures of cristobalite and corundum on a platinum-40 rhodium strip furnace. The latter two methods do not always yield a homogeneous product, and the index of refraction of those glasses is variable. The straight line in Fig. 4 is based on the three points obtained by the quenching method and is used in conjunction with the Schairer and Bowen (1955) data to construct Fig. 5. The index of refraction of a glass of the anhydrous muscovite composition is estimated to be about 1·516. It appears as though the glasses prepared on the graphite-resistor furnace lost SiO_2 by reduction to silicon. The composition of the glass therefore must lie close to anhydrous muscovite on an extension of the join anhydrous muscovite—quartz.

At the request of the writers, Dr. M. L. Keith of Pennsylvania State University melted a muscovite from the Welch Mine, Macon Co., N.C. (U.S.N.M. 18205). The sample was preheated for eighteen hours at 1200°C, ground, and sealed in platinum-20 rhodium tubes. He obtained the following results:

Temp., °C	*Time, min*	*n glass*
1850	1	1·524
1715	10	1·521*

* Glass contained 10 per cent corundum (?) crystals.

In preliminary experiments he observed that muscovite melted in air on a platinum-40 rhodium strip furnace bubbled at temperatures between 1700°C and 1720°C. The best estimate of the index of refraction of a glass of the anhydrous muscovite composition is given by Keith as 1·522.

(d) Leucite from Vesuvius, Italy (U.S.N.M. 104486), was mixed with sillimanite from the Benson Mine, N.Y., in the proportions equivalent to anhydrous muscovite. Both materials

were carefully purified by Th. G. Sahama and K. Neuvonen, analysed by von Knorring, and used for calorimetry by F. C. Kracek (1954, unpublished). Intimate mixing was obtained by grinding in acetone for one hour.

(e) Muscovite lies in the triangle montmorillonite—$K_2O \cdot Al_2O_3$—kaolinite when the compositions of the compounds are projected onto the anhydrous plane. A montmorillonite of the American Petroleum Institute Clay Mineral Standards Collection (Kerr *et al.*, 1950b, p. 50) from Polkville, Miss., and the Zettlitz kaolinite described above, were used. The $K_2O \cdot Al_2O_3$ was prepared by the second method described by Fricke and Jucaitis (1930, p. 142). These materials were ground in acetone for two hours.

(f) Muscovite also lies in the triangle quartz—$K_2O \cdot Al_2O_3$—kaolinite when the compounds are projected onto the anhydrous plane. Silica glass prepared by W. C. Heraeus, potassium aluminate, and the Zettlitz kaolinite, were mixed in the proper proportions and ground together in acetone for two hours.

(g) The anhydrous composition of muscovite lies on the join sanidine—corundum not shown in Fig. 2 or Fig. 3. Mix (a) or glass (c) was held at 700°C and 15,000 p.s.i. for twenty-four hours in order to produce a fine-grained mixture of sanidine + corundum.

(h) Batches of synthetic 1Md muscovite were prepared from the orthorhombic $KAlSiO_4$ + kaolinite mixture by holding it for two to seven days at about 600°C and 15,000 p.s.i.

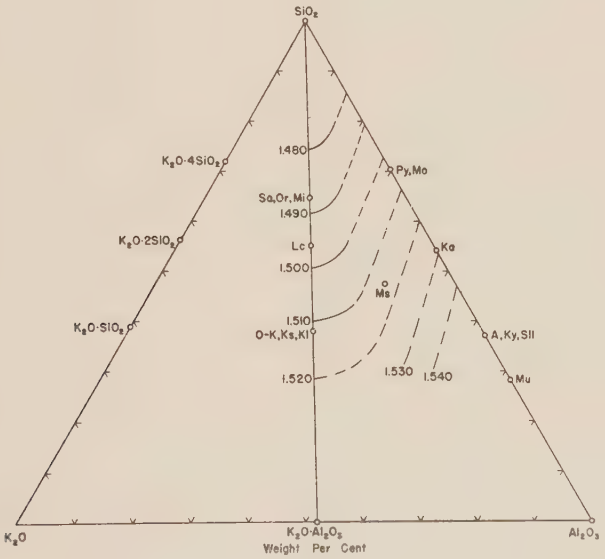


Fig. 5. Isofracts for a portion of the K_2O—Al_2O_3—SiO_2 system based on work of Schairer and Bowen (solid curves) and on data in Fig. 4.

In addition to the above mixtures, several natural muscovites were used as starting materials.

(i) 1M muscovite, Sarospatak, Hungary. The clay mica described by Maegdefrau and Hofmann (1938a) and later called sarospatakite (Sedletsky, 1940) was obtained through the courtesy of George Faust from Ulrich Hofmann. The X-ray powder pattern taken of the material received and the spacings published by Maegdefrau and Hofmann both indicate that the material is a mica having a 1M structure. The basal spacing appears to be slightly larger than that for pure muscovite. According to Grim, Bradley, and Brown (Brindley, 1951, p. 152), sarospatakite is "roughly intermediate between illite and montmorillonite" on the basis of indices of refraction and differential thermal analysis curves. Those authors describe the sarospatakite as an "inter-layer mixture." Mackenzie, Walker, and Hart (1949, p. 711) discuss the DTA evidence regarding the possibility that sarospatakite is a mixture, and conclude from their studies that the thermal peak assigned to montmorillonite (Grim and Rowland,

1942, p. 753) is also present in some illites. George Faust (1955, unpublished data) found from his DTA studies that sarospatakite is chiefly a hydromica, but may have some montmorillonite. In view of these data it is concluded that the material from Sarospatak is a 1M muscovite with a minor amount of interlayer montmorillonite.

(j) Mixed-layer 1Md + montmorillonite and 2M muscovite, Fithian, Illinois. The material is described by Grim, Bray, and Bradley (1937), and is listed as a typical illite. On the basis of X-ray patterns of a sample obtained from R. E. Grim, the Fithian illite contains mixed-layer 1Md + montmorillonite and 2M muscovite. Another purified sample obtained through the courtesy of P. Kerr was also found to be a mixture.

(k) 2M muscovite, Spruce Pine, N.C. (U.S.N.M. 96460). Books of the mica were filed on edge and ground for two hours dry.

(l) 2M muscovite, Spruce Pine, N.C. (U.S.N.M. 96460). Books of the mica were filed on edge and ground for four hours dry.

(m) 2M muscovite, Spruce Pine, N.C. (U.S.N.M. 96460). Books of mica were filed on edge and ground for thirty hours dry.

(n) 3T muscovite, Ballater, Aberdeen, Scotland. The illite described by Mackenzie, Walker, and Hart (1949) was found by the present writers to have a 3T structure. The X-ray powder data published were compared by them with materials called illite and hydromuscovite, now known to have the following structures:

Name	*Locality*	*Description*	*Structure*
Illite	South Wales	Nagelschmidt and Hicks, 1943	3T
Illite	Gilead, Ill.	Grim, Bray, and Bradley, 1937	2M
Hydromuscovite	Ogofau, Wales	Nagelschmidt, 1937[2]	1M

The variety of structure accounts for the difficulty encountered by Mackenzie, Walker, and Hart in matching the spacings. The indices published are based on a two-layer structure, and should refer only to the Gilead, Illinois, material. A $<1{\cdot}4\ \mu$ fraction of the Ballater illite supplied by R. C. Mackenzie was used in the present study.

(o) 3T muscovite, Sultan Basin, Washington. The structure was originally identified as 3M by Axelrod and Grimaldi (1949), but later was shown by Smith and Yoder (1955) and by Levinson (1955) to be 3T. A portion of the material studied by Axelrod and Grimaldi was ground in acetone for four hours for use in the hydrothermal experiments.

Apparatus

The equipment necessary to maintain the initial materials at a fixed temperature and pressure for extended periods of time is described in a previous publication (Yoder and Eugster, 1954, p. 160). The samples were contained in either platinum foil crucibles or sealed platinum tubes. The runs in which the latter container was used are marked with an asterisk in the data tables.

Identification of Products

The very fine-grained nature of the products usually obtained in hydrothermal experimentation required use of X-ray diffraction, or electron microscope techniques, for identification of the phases. The petrographic microscope was employed when the initiation of a reaction was being investigated, or whenever the products were sufficiently coarse-grained.

The Norelco Geiger-counter diffractometer, capable of recording the back-reflection region, was used for the powder X-ray techniques. The powdered samples were mounted on a glass slide using acetone as a mounting medium or dusted into a shallow aluminium cell. Some of the

[2] The published Ogofau, Wales, hydromuscovite X-ray data list one strong reflection at 2·89 Å, which appears in the 3T structure. A principal reflection for the 3T structure of approximately the same intensity at about 3·87 Å is not present. The principal reflection of dolomite also has the 2·89 Å spacing. Dolomite has been found to occur with at least one "illite" from the Gunflint iron formation, Ontario. The chemical analysis of the Ogofau material indicates that the CO_2 content is nil; however, the method of releasing possible gas was not mentioned. It is believed that the chemical analysis does not exclude the possibility that dolomite was present in the sample.

natural micas were filed, ground in acetone, and the −325-mesh fraction placed in the cell mount. Some preferred orientation was observed for materials mounted in this way. The synthetic products, being very fine-grained, presented no preferred orientation problems.

Electron microscopy and selected area diffraction studies were made by Max Swerdlow of the Constitution and Microstructure Section, National Bureau of Standards. The specimens were prepared for study by Dr. Swerdlow in the following way. About 10 mg of the dry material were briefly ground in about 1 cc of butyl alcohol in a mullite mortar in order to break up large aggregates of material. Drops of the alcohol slurry were agitated by shaking in the pipette used to transfer the material. One drop was placed on a collodion-covered stainless-steel specimen screen (200-mesh), and allowed to dry in a room air-conditioned at 23°C and 50 per cent relative humidity. The specimens were then examined with a 50 kV R.C.A. Electron Microscope Type EMV–2C modified for selected area diffraction.

Experimental Results

Hydrothermal Data

The hydrothermal experiments in which the composition of the initial materials approached the hydrous or anhydrous equivalent of muscovite are given in Table 2. The abbreviations used to designate the phases are defined in Table 1. The

Table 1. *Abbreviations used to designate phases*

A	Andalusite	Mi	Microcline
Bo	Boehmite	Mo	Montmorillonite
C	Corundum	Ms	Muscovite
Co	Cordierite	Mu	Mullite
Cr	Cristobalite	O-K	Orthorhombic $KAlSiO_4$
D	Diaspore	Or	Orthoclase
F-Ms	Fluoromuscovite	Py	Pyrophyllite
G	Gibbsite	Q	Quartz
Ka	Kaolinite	Sa	Sanidine
Kl	Kaliophilite	Sil	Sillimanite
Ks	Kalsilite	To	Topaz
Ky	Kyanite	Tr	Tridymite
L	Liquid	V	Vapour
Lc	Leucite		

sanidine obtained in the experiments was determined by Wm. S. MacKenzie on the basis of X-ray powder patterns as the high-temperature form. It will

be considered in the discussions to follow as equivalent to low-temperature sanidine, microcline, or orthoclase, in those regions of temperature and pressure where one of these phases is the more stable form. When the polymorphic form of muscovite has been determined, the symbol of muscovite, Ms, is preceded by the number of layers and the symmetry symbol of the unit cell. The interpretation of the data in Table 2 is not always straightforward, and a few comments on the results from each starting material are desirable.

(a)* Muscovite grows from these materials up to 500° ± 50°C at 15,000 p.s.i. Above this temperature and below 925° ± 5°C, sanidine + corundum + vapour appear to be the stable phases. Above 925°C melting takes place, and the phases in equilibrium with liquid and vapour are leucite + corundum. The leucite in the run of short duration at 910°C is believed to be evidence of metastable growth rather than leaching of SiO_2. No glass was observed to indicate that the incongruent melting of sanidine had taken place. For the system $KAlSi_3O_8$—H_2O, the incongruent melting of sanidine takes place at 990°C under 15,000 p.s.i. water pressure, according to Goranson (1938, p. 89). As is demonstrated below, the products from the runs at 600°C and 625°C are metastable.

(b) The long runs in sealed tubes at 2000 p.s.i. water pressure indicate that the stable phases in the temperature range investigated are Sa + C + V. It was anticipated that the assemblage Sa + Mu + Lc + V would be encountered at the highest temperatures in accord with the results of the anhydrous system investigated by Schairer and Bowen (1955). It is known from the work of Goranson (1938) that the field of leucite rapidly diminishes with increasing water pressure, and it appears though the field of stability of mullite is greatly restricted even by low water pressures. Muscovite grows from this mixture up to approximately 630°C at 5000 p.s.i. water pressure. The metastable growth of Sa + C in the region where muscovite grows is clearly indicated. At 10,000 p.s.i. water pressure, muscovite appears to grow up to about 650°C, where Sa + C + V become the stable phases. The growth of muscovite under 15,000 p.s.i. water pressure takes place up to about 670°C where Sa + C + V are stable. The series of runs at 910°C indicate two interesting features of hydrothermal growth in open capsules. The run of one hour shows that, for this starting material, leucite grows faster than sanidine and appears metastably. With longer runs leucite reacts with the remaining material to give the stable compound sanidine. With still longer runs (128 hours) the silica is leached out of the capsules, in spite of the large buffer, and leucite again appears in the products. At 935° ± 5°C at 15,000 p.s.i. water pressure, sanidine melts incongruently to Lc + C + L + V. At 30,000 p.s.i. water pressure the mica grows up to about 700°C, and then Sa + C + V appear to be the stable phases. Between 900°C and 930°C, sanidine melts congruently.

(c) It would appear on first inspection of these runs that the upper stability limit for muscovite at 15,000 p.s.i. water pressure is 625° ± 5°C. However, the growth of mica, if only in trace amounts above this temperature, indicates that it is stable at least up to 665° ± 5°C. Although it is common for minerals to grow metastably below their lower stability limit, metastable growth above their upper

* Letters refer to sections of Table 2.

Table 2. Results of hydrothermal treatment of various charges of the muscovite composition

Temp. °C	*Pressure* $\times 10^{-3}$ *p.s.i.*	*Time hours*	*Products*
		(a) $K_2O \cdot 6SiO_2$ glass + γ-Al_2O_3 + H_2O	
*350	15	1460	1M-Ms
400	15	187	1M-Ms
500	15	144	1M-Ms
600	15	24	Sa + C (?)
600	15	166	Sa + C
625	15	24	Sa + C
700	15	24	Sa + C
800	15	23	Sa + C
900	15	24	Sa + C
900	15	24	Sa + C
910	15	9	Sa + Lc + C
910	15	38	Sa + C
920	15	19	Sa + C
930	15	21	Lc + C + glass
950	15	13	Lc + C + glass
		(b) O—K + Ka + H_2O	
800	2	4	Lc + Sa + C + (?)
*800	2	171	Sa + C
850	2	4	Lc + Sa + C + (?)
*850	2	167	Sa + C
900	2	4	Lc + Sa + C + (?)
900	2	165	Sa + C + Lc
*900	2	171	Sa + C
925	2	4	Lc + Sa + C
960	2	4	Lc + C + (?)
980	2	4	Lc + C + (?)
1000	2	4	Lc + C + (?)
*1000	2	167	Sa + C + Lc (?)
580	5	308	1M-Ms + Sa + C (?)
600	5	330	1M-Ms + Sa + C
620	5	334	1M-Ms + Sa + C
630	5	477	Ms + Sa + C
630	5	505	Sa + C
610	7·5	189	1M-Ms + Sa + C (?)
635	10	184	1M-Ms + Sa + C (?)
650	10	336	Sa + C + Ms (tr)
*200	15	4120	1M-Ms
*350	15	1460	1M-Ms
*350	15	2208	1M-Ms + 2M-Ms
400	15	144	1Md-Ms
*500	15	888	1M-Ms + 2M-Ms + 3T-Ms (?)
600	15	48	1M-Ms
630	15	160	1M-Ms
630	15	168	1Md-Ms
650	15	168	1M-Ms
*650	15	780	1M-Ms + 2M-Ms
660	15	47	1M-Ms + Sa + C (?)

Table 2 (continued)

Temp. °C	*Pressure* $\times 10^{-3}$ *p.s.i.*	*Time hours*	*Products*
		(b) O—K + Ka + H_2O (*contd.*)	
660	15	169	1M-Ms + Sa + C (?)
670	15	181	Sa + C + Ms (tr)
680	15	161	Sa + C
900	15	24	Sa + C
910	15	1	Lc + C + ?
910	15	5	Sa + C
910	15	16	Sa + C
910	15	24	Sa + C
910	15	128	Sa + C + Lc
920	15	23	Sa + C
930	15	21	Sa + C
940	15	22	Lc + C + glass
950	15	30	Lc + C + glass
1000	15	6	Lc + C + glass
680	22·5	330	Ms + Sa + C
700	22·5	336	Sa + C
*600	30	861	1M-Ms + 2M-Ms
*650	30	216	1M-Ms + 2M-Ms
*650	30	332	1M-Ms + 2M-Ms
680	30	64	1M-Ms + Sa + C (?)
*680	30	812	2M-Ms + 1M-Ms
690	30	498	2M-Ms
700	30	70	Sa + C + Ms
*700	30	330	Sa + C
710	30	72	Sa + C
710	30	163	Sa + C
900	30	6	Sa + C
930	30	1	C + glass
		(c) Glass + H_2O	
*350	15	1460	1Md-Ms
†*350	15	1460	1Md-Ms
400	15	164	1Md-Ms
500	15	47	1M-Ms
600	15	24	1M-Ms
600	15	67	1M-Ms
610	15	137	1M-Ms + Sa + C
620	15	188	1M-Ms + Sa + C
630	15	22	Sa + C
630	15	137	Sa + C
640	15	24	Sa + C
650	15	24	Sa + C + Ms (tr)
660	15	40	Sa + C + Ms (tr)
670	15	47	Sa + C
680	15	111	Sa + C
700	15	24	Sa + C
900	15	15	Sa + C

Table 2 (continued)

Temp. °C	*Pressure* $\times 10^{-3}$ *p.s.i.*	*Time hours*	*Products*
		(d) Lc + Sil + H_2O	
*350	15	1460	1M-Ms
650	15	48	Sil + Lc + Sa + Ms
900	15	76	Sa + C
*600	30	1826	1M-Ms + Sil + Sa + ?
650	30	336	1M-Ms
*800	30	1826	Sa + C
		(e) Mo + $K_2O \cdot Al_2O_3$ + Ka + H_2O	
400	15	90	1Md-Ms
500	15	25	1M-Ms
*500	15	717	1M-Ms
600	15	17	1M-Ms + Sa + C (?)
600	15	167	Ms + Ks + ?
650	15	170	Ms + Sa + C
*650	15	780	1M-Ms + Sa + C
*600	30	861	1M-Ms
		(f) Q + $K_2O \cdot Al_2O_3$ + Ka + H_2O	
*200	15	4120	1Md-Ms + Ka + ?
*350	15	2208	1Md-Ms + Ka + ?
400	15	89	1Md-Ms
500	15	17	1Md-Ms
*500	15	717	1M-Ms + 2M-Ms (tr)
600	15	24	1M-Ms
600	15	94	1M-Ms
650	15	141	1M-Ms + 2M-Ms
310	30	17	1Md-Ms + Ka + ?
450	30	23	1Md-Ms
*600	30	861	1M-Ms + 2M-Ms
		(g) Sa + C + H_2O	
*350	15	1460	1Md-Ms + C + Sa (?)
600	15	160	Sa + C
600	15	166	Sa + C
		(h) 1Md-Ms + H_2O	
600	5	287	1M-Ms + Sa (tr)
620	5	334	1M-Ms
650	5	506	Sa + C + Ms
650	10	185	1M-Ms + Sa (tr)
610	15	163	1M-Ms + Sa (tr)
680	15	334	1M-Ms + Sa + C
*700	15	625	Sa + C
700	30	168	1M-Ms + Lc + C + Sa (tr)
710	30	168	2M-Ms + 1M-Ms
710	30	182	2M-Ms + 1M-Ms
725	30	94	Sa + C + 1M-Ms

Table 2 (continued)

Temp. °C	*Pressure* $\times 10^{-3}$ *p.s.i.*	*Time hours*	*Products*
		(i) Natural 1M-Ms	
*350	15	1460	1M-Ms
*500	15	888	1M-Ms + 2M-Ms
600	15	156	1M-Ms + Co
625	15	24	1M-Ms
650	15	23	1M-Ms + Co + Sa + Mu
650	15	190	1M-Ms + Co + Sa + Mu
700	15	164	Sa + Co + Mu
*600	30	861	1M-Ms + 2M-Ms
*690	30	336	2M-Ms + 1M-Ms (tr) + Q
		(j) Natural 1M-Ms + 2M-Ms	
600	15	132	1M-Ms + 2M-Ms (tr) + Co + Q
*600	30	861	2M-Ms
		(k) Natural 2M-Ms (ground 2 hours)	
*350	15	1460	2M-Ms
600	15	140	2M-Ms
650	15	340	2M-Ms
*650	15	780	2M-Ms
660	15	91	2M-Ms
670	15	332	Sa + C + Ms
700	15	68	Sa + C + Ms
800	15	47	Sa + C + Ms
900	15	24	Sa + C
		(l) Natural 2M-Ms (ground 4 hours)	
650	15	165	2M-Ms + 1M-Ms
600	30	142	1M-Ms + 2M-Ms
*700	30	330	2M-Ms
		(m) Natural 2M-Ms (ground 30 hours)	
*350	15	1460	1Md-Ms + $Q^{\ddagger}_{\ddagger}$
600	15	162	1M-Ms
600	15	160	1M-Ms + 2M-Ms (tr)
625	15	24	1M-Ms + 2M-Ms + $Q^{\ddagger}_{\ddagger}$
650	15	160	1M-Ms + 2M-Ms + Sa + $Q^{\ddagger}_{\ddagger}$
*650	15	780	Sa + C + Ms
		(n) Natural 3T-Ms (Scotland)	
*500	15	717	3T-Ms
*650	15	780	2M-Ms + 3T-Ms
*600	30	861	2M-Ms + 3T-Ms
*690	30	336	2M-Ms + 3T-Ms + Q

Table 2 (continued)

Temp. °C.	*Pressure* $\times 10^{-3}$ *p.s.i.*	*Time hours*	*Products*
		(o) Natural 3T-Ms (Washington)	
650	15	167	3T-Ms
*650	30	172	3T-Ms
*650	30	408	3T-Ms + 2M-Ms (tr)
*650	30	2286	2M-Ms + 3T-Ms
*650	30	2286	2M-Ms + 3T-Ms
680	30	354	2M-Ms + Sa + C (?)
*700	30	330	Sa + C

* Sealed platinum tube.
† Glass prepared from natural muscovite.
‡ Quartz probably derived from agate mortar.

stability limits has not been observed. As mentioned above, the glass may not have been of the proper composition; however, the results support the contention that the composition lies close to that of muscovite.

(d) The partial reaction of sillimanite and leucite with water to yield a mica in the short time of forty-eight hours, as well as their complete reaction at 350°C, was not anticipated by the writers. The chief purpose in performing experiments with this particular mixture was to test the validity of the join Sa + C + V above the stability range of muscovite. The fact that Sa + C + V was obtained clearly establishes that assemblage as more stable than Lc + Mu + V or Lc + Sil + V (see Fig. 3).

(e) and (f) The incompleteness of reaction is exhibited in several runs of these mixtures. Kaolinite persisted even though it contains structural features similar to those of the mica.

(g) The principal point of these runs was to test the reversibility of the reaction Ms $\rightleftharpoons$ Sa + C + V deduced from other runs. It is seen that only with the very long run at 350°C was reversibility demonstrated. It would be expected that, with longer runs at 600°C, muscovite would also have been produced. Experience in other systems has indicated that corundum, once formed, is very slow to react.

(h) Further proof of the reversibility of the reactions Ms $\rightleftharpoons$ Sa + C + V is found in the runs in which synthetic Ms decomposes to Sa + C + V. At 5000 p.s.i. water pressure muscovite decomposes at 635° $\pm$ 15°C. Muscovite is clearly breaking down between 610°C and 680°C at 15,000 p.s.i. water pressure. At 30,000 p.s.i. the decomposition is fixed at 715° $\pm$ 10°C. Leaching of silica is evident in one run, and traces of sanidine appear metastably below the decomposition in several runs.

(i)–(o) The experiments on the various natural muscovite polymorphs of unknown composition support the results obtained from the synthetic mixtures. In addition, some notion of the composition of the natural micas can be gained from the hydrothermal experiments. For example, the micas from Sarospatak (Hungary) and Fithian (Illinois) both yielded a mineral containing magnesium, cordierite. One may conclude that the original sample was not purified completely;

random interstratification with a Mg-bearing layered mineral existed, or magnesium was present in a celadonite-type mica structure. It also appears as though the sample was not homogeneous, because quartz is observed in some runs and not in others. Quartz was not observed in the X-ray patterns of the original material; however, it may have been too fine-grained to be resolved by X-rays. The writers suggest that hydrothermal treatment of fine-grained minerals and rocks may serve as a general method for aiding in their identification, and for contributing to the knowledge of their composition.

It should be stated clearly that considerable judgment on the part of the experimenters is involved in the interpretation of the results. The final analysis

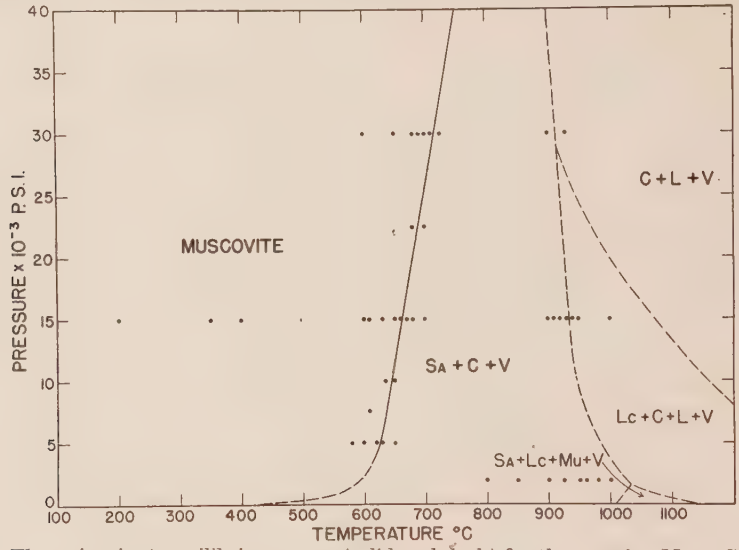


Fig. 6. The univariant equilibrium curve (solid and dash) for the reaction Ms $\rightleftharpoons$ Sa + C + V, estimates of the equilibrium curves for the melting of sanidine and leucite (dash) in the muscovite composition, and one possible relation between the assemblages Sa + C + V and Mu + Sa + Lc + V.

of the data on the synthetic starting materials (b) and (h), which are believed to have produced the most reliable results, is given in Fig. 6. The solid curve represents the equilibrium conditions of the reaction:

Muscovite $\rightleftharpoons$ sanidine + corundum + vapour.

The dashed portion of that univariant curve is obtained by calculations presented in a section below on thermodynamics. The completely dashed curves at higher temperatures represent estimates based on the experimental data and on the work of Goranson (1938) of the equilibrium conditions for the melting of sanidine and leucite, as well as the possible relations between the assemblages Sa + C + V and Mu + Sa + Lc + V.

Description of Synthetic Muscovites

A photomicrograph of a representative sample of the muscovite obtained from the hydrothermal treatment of the various mixtures as seen under the petrographic microscope is given in Fig. 7. The average size of the crystals obtained is less than

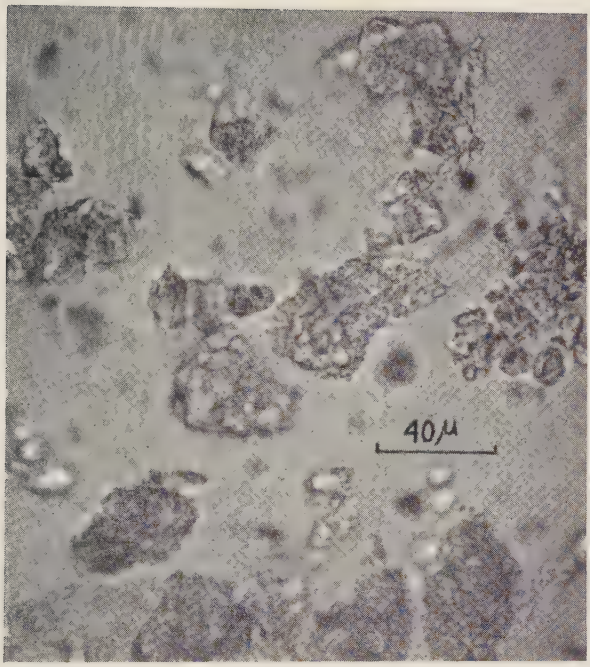
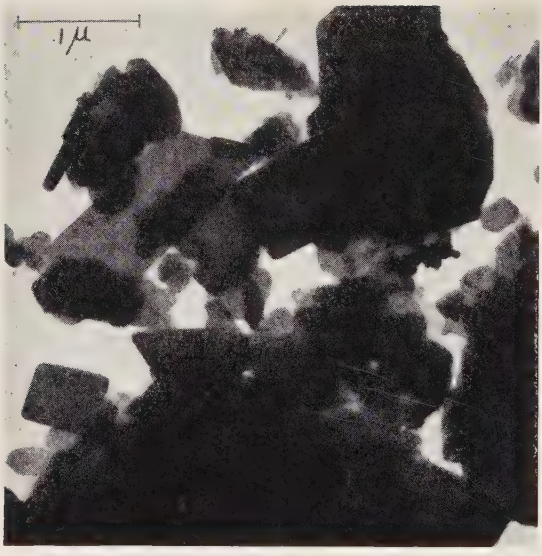
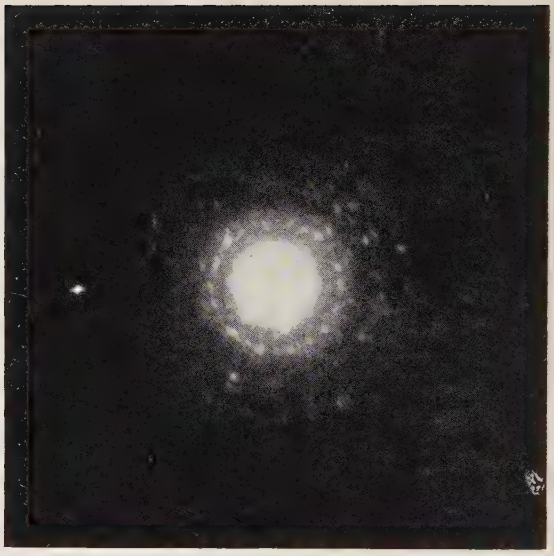


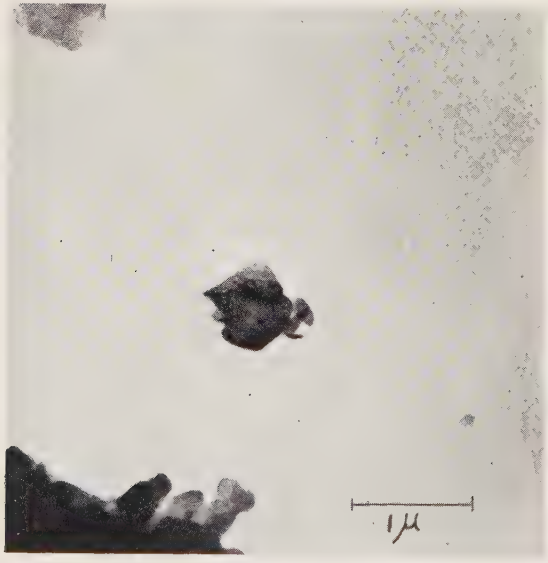
Fig. 7. Photomicrograph of a representative sample of synthetic hydroxyl-bearing muscovite.



(a)



(b)



(c)

(d)

Fig. 8. (a) Electron-micrograph of synthetic 1M muscovite made from O—K + Ka + H_2O at 620°C, 5000 p.s.i., 334 hours. Taken by MAX SWERDLOW, National Bureau of Standards.
(b) Transmission-selected area-diffraction pattern of a portion of the field shown in (a).
(c) Electron-micrograph of an isolated aggregate of synthetic 1M muscovite shown in (a).
(d) Transmission-selected area-diffraction pattern of synthetic 1M muscovite shown in (c).

5 microns, and the largest crystals observed were about 20 microns in diameter. The individual crystals when observable were usually thin, irregular plates having wavy extinction. It was not possible to obtain an interference figure on the minute crystals. The birefringence was weak on the plate and very strong on edge. The approximate index of refraction on the plate was close to 1·58. These optical properties are in accord with those expected for muscovite.

Under the electron microscope the synthetic muscovite appears as in Fig. 8a. The largest crystals in the electron-micrograph are about $1 \times 2\mu$ and, judging from their transparency, less than 100 Å thick. For these particular crystals, which have the 1M structure, some of the individuals consist of a stack less than 10-unit cells thick. The trace of the prism faces on some of the basal plates makes

Table 3. *X-ray powder data for a synthetic* 1*M muscovite*

$2\theta_{obs}$	$Q_{obs} \times 10^5$	$\Delta Q \times 10^5$	*hkl*	*I*	*d*
8·775	985	2	001	>100	10·077*
17·610	3943	5	002	37	5·036*
19·780	4964	−20	020	90	4·488*
20·420	5287	−4	11$\bar{1}$	27	4·349
21·595	5905	26	021	16	4·115
24·315	7463	−1	11$\bar{2}$	60	3·660
26·560	8879	4	003	>100	3·356*
		13	022		
29·055	10589	1	112	50	3·073
30·515	11654	−39	11$\bar{3}$	6	2·929
33·310	13823	4	023	16	2·689
34·745	15002	−36	130	50	2·582*
34·980	15199	−28	13$\bar{1}$	90	2·565
35·200 ?	15385	−17	200	22	2·550*
36·680	16660	75	131	11	2·450
37·385	17284	26	13$\bar{2}$	4	2·405
37·800	17656	86	11$\bar{4}$	12	2·380
40·155*b*	19831	−55	040	8	2·246
40·650*b*	20302	10	220	7	2·219
41·200 ?	20831	−68	041	4	2·191
41·900*b*	21513	−10	13$\bar{3}$	20	2·156
42·870	22474	−30	202	6	2·109
45·035	24681	−6	005	32	2·013*
46·400*b*	26113	82	133	7	1·957
47·860*b*	27692	−62	13$\bar{4}$	4	1·900
55·045	35934	−16	11$\bar{6}$	18	1·668
55·590*b*	36593	−79	151	12	1·653
56·250*b*	37394	22	204	12	1·635
61·210 ?	43615	−64	135	4	1·514
61·885	44492	−4	060	33	1·499*

$2\theta_{obs}$ in degrees: Cu$K\alpha$ $\lambda = 1{\cdot}5418$ Å
b = broad peak
d = interplanar spacing in Å
$Q = 1/d^2$
$\Delta Q = Q_{calc} - Q_{obs}$
I = relative intensity based on arbitrary linear scale
* Peaks observed in 1Md muscovite.

an angle of 60°. The transmission-selected-area-electron-diffraction pattern of a portion of the field shown in Fig. 8a is given in Fig.8b. The pattern shows preferred orientation of the crystals which were insufficient in number to fulfil the Debye-Scherrer rings. The interplanar spacings are similar to those obtained by means of X-ray powder diffraction analysis (see next section). An electron-micrograph of an isolated aggregate of synthetic muscovite is given in Fig. 8c. The variations in apparent thickness are due to either overlapping platy particles, layering, or changes in density of the mass. The transmission-selected area-electron-diffraction pattern of this aggregate is given in Fig. 8d. The hexagonal symmetry is obvious from the cross-grating pattern obtained from the two-dimensional single crystal which apparently dominates the aggregate. The variation in intensity of the spots may be attributed in part to variations of thickness or density.

As will be apparent from the following discussions, knowledge of the K_2O and H_2O content of the synthetic muscovite is required. The potash content of two 20-mg samples, carefully prepared in sealed tubes at 650°C and 30,000 p.s.i. water pressure for 430 hours, was determined by the flame-photometer method. The K_2O contents were 11·7 per cent and 12·1 per cent, and the error is believed to be $\pm$0·5 per cent. The water content of the same samples was 4·52 per cent and 4·27 per cent, respectively, and the error of measurement is $\pm$0·2 per cent. The water and potash contents of an ideal muscovite are 4·52 per cent and 11·83 per cent, respectively.

Polymorphism

X-ray powder patterns were made for the identification of the synthetic muscovite polymorphs. Photographs, taken by the present writers, of X-ray powder patterns of natural polymorphs of muscovite which have been previously recognized, the common 2M and the rarely observed 3T, are given in Fig. 9. The first micaceous products obtained in this investigation had neither the 2M nor the 3T structures. For this reason an attempt was made to index the powder pattern of synthetic mica (Fig. 9, synthetic 1M) on the basis of the one-layer cell. The results are given in Table 3. It was concluded from these data that the first synthetic micas obtained in this investigation had a 1M structure with the following cell constants:

$$a = 5{\cdot}208 \pm 0{\cdot}010 \text{ Å}$$
$$b = 8{\cdot}995 \pm 0{\cdot}020 \text{ Å}$$
$$c = 10{\cdot}275 \pm 0{\cdot}005 \text{ Å}$$
$$\beta = 101° 35' \pm 5'.$$

Efforts were then made to produce the 2M and 3T polymorphs by holding the synthetic mixtures for long periods of time at conditions close to the upper stability limit. The sequence of growth as depicted by the X-ray powder patterns is given in Fig. 10. The 1Md mica commonly obtained at the lowest temperatures or in runs of short duration is represented by the bottom pattern in the figure. In some runs all the *hkl*'s were absent, and this was interpreted as evidence of complete disorder of the layers. The nature of the disorder has been described by Hendricks and Jefferson (1939) and amplified by Smith and Yoder (1955). As greater order of

the layers is obtained, the *hkl*'s appear, and the intensity of these may be used as a measure of the amount of remaining disorder. In particular, the $11\bar{2}$ and 112 reflections are useful for this purpose.[3] With increasing temperature and duration of run, growth usually results in a completely ordered 1M. Subsequently the the 1M structure is superseded by the 2M structure represented by the top pattern in Fig. 10. This sequence of growth was observed to take place even at the highest temperatures. It is concluded, therefore, that the 2M structure is more stable at the higher temperatures than the 1M structures. In order to test this conclusion,

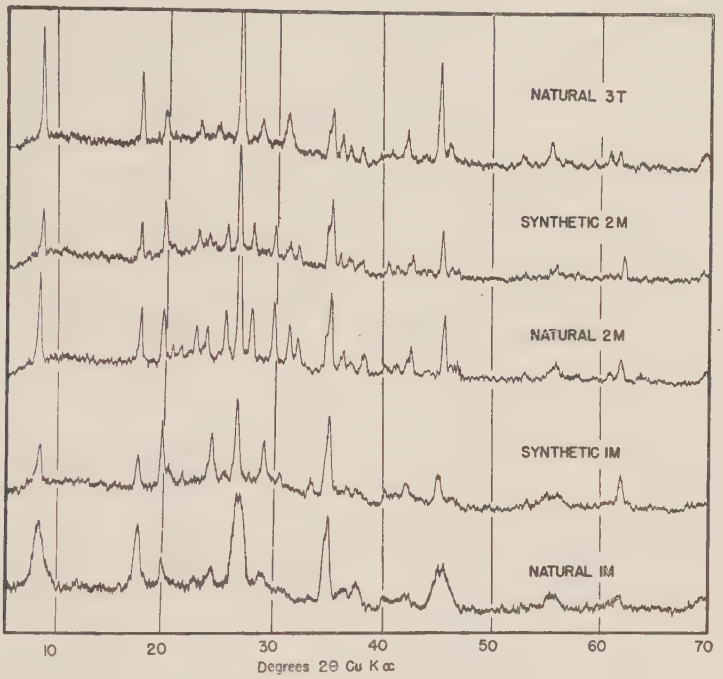


Fig. 9. Photograph of X-ray powder patterns of the following micas (from top to bottom):
Natural 3T. Sultan Basin, Snohomish County, Washington (Axelrod and Grimaldi, 1949).
Synthetic 2M. Made from O—K + Ka + H_2O at 690°C and 30,000 p.s.i. for 498 hours.
Natural 2M. Spruce Pine, N.C. (U.S.N.M. 96460).
Synthetic 1M. Made from O—K + Ka + H_2O at 200°C and 15,000 p.s.i. for 4120 hours in a sealed platinum tube.
Natural 1M. Sarospatakite from U. Hofmann through the courtesy of G. Faust.

it was necessary to obtain samples of the natural polymorphs and subject them to a series of similar conditions. (The identification of natural 1Md and 1M polymorphs is given in detail in the next section.) The results are given in Tables 2(i) through 2(o). The persistence of the 2M structure at low temperatures is believed to be due to the slow rate of inversion. At high temperatures the 1M and 3T structures inverted to 2M, and the 2M structure remained unchanged. Although it was not possible to demonstrate reversibility, the evidence supports the conclusion

[3] Great care must be exercised in applying this method to some natural micas. The small size and random growth of the synthetic micas reduce preferred orientation common to the large, orientated natural micas.

that the 2M structure is the most stable form at high temperatures. The temperatures and pressures at which the 3T polymorph is stable cannot be delineated with the data at hand. It may be that factors other than pressure and temperature control the growth of the 3T structure (see Smith and Yoder, 1955). The appearance of the 1Md structure as the initial phase at all temperatures in some starting materials suggests that it is a metastable form; however, its subsequent ordering and persistence at the low temperatures indicate that the 1M mica

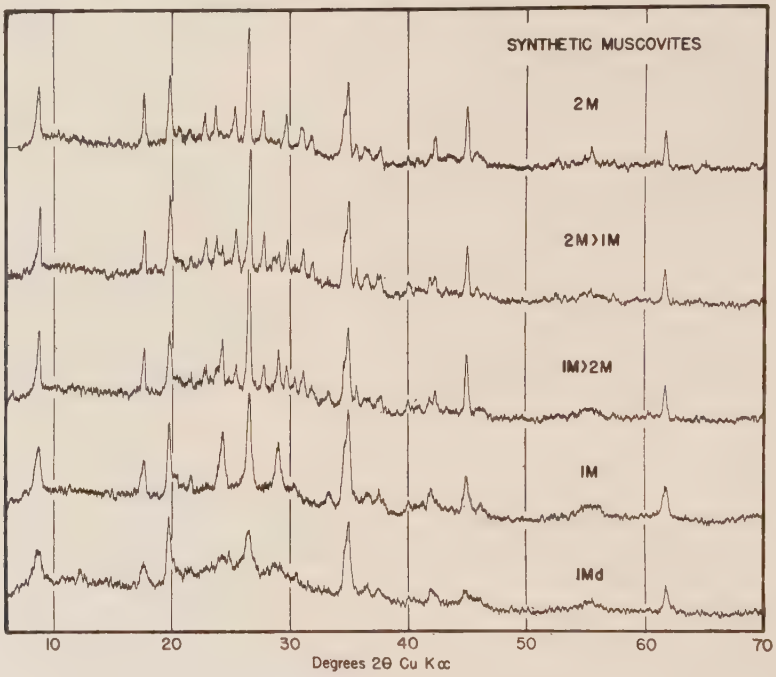


Fig. 10. Photograph of X-ray powder patterns of the following synthetic muscovites prepared from O—K + Ka + H_2O (from top to bottom):

2M: 690°C at 30,000 p.s.i. for 498 hours
2M > 1M: 710°C at 30,000 p.s.i. for 168 hours
1M > 2M: 710°C at 30,000 p.s.i. for 182 hours
1M: 200°C at 15,000 p.s.i. for 4120 hours
1Md: prepared from Ka + Q + $K_2O \cdot Al_2O_3$ + H_2O. 200°C at 15,000 p.s.i. for 4120 hours.

is a stable polymorph. On the basis of long runs (Table 2(b)) the transition of 1M to 2M appears to be between 200°C and 350°C at 15,000 p.s.i. water pressure.

The powder patterns of the synthetic 1M and 2M polymorphs are compared with those of the natural 1M and 2M polymorphs in Fig. 9. The close agreement is readily discernible. The indices of the X-ray powder pattern of the synthetic 2M muscovite are given in Table 4, and the parameters of the unit cell are as follows:

$$a = 5{\cdot}189 \pm 0{\cdot}010 \text{ Å}$$
$$b = 8{\cdot}995 \pm 0{\cdot}020 \text{ Å}$$
$$c = 20{\cdot}097 \pm 0{\cdot}005 \text{ Å}$$
$$\beta = 95° 11' \pm 5'.$$

Table 4. X-ray powder data for a synthetic 2M muscovite

$2\theta_{obs}$	$Q_{obs} \times 10^5$	$\Delta Q \times 10^5$	*hkl*	*I*	*d*
8·830	997	−7	002	>100	10·014
17·665	3963	−1	004	55	5·021
19·825	4986	−5	110	55	4·478
19·915	5032	3	$11\bar{1}$	65	4·458
20·225	5187	4	021	14	4·391
20·675	5419	4	111	21	4·296
21·625	5922	12	022	14	4·109
22·375	6335	24	112	12	3·973
22·865	6611	14	$11\bar{3}$	37	3·889
23·820	7167	5	023	32	3·735
25·450	8165	2	$11\bar{4}$	44	3·500
26·600	8906	8 2	006 024	>100	3·351
27·810	9718	1	114	47	3·208
29·795	11122	12	025	47	2·999
31·160	12139	2	115	35	2·871
31·925	12727	4	$11\bar{6}$	22	2·803
34·640	14914	8	$13\bar{1}$	50	2·589
34·770	15023	35	116	45	2·580
35·025	15237	−43	$20\bar{2}$	90	2·562
35·720	15828	18	008	20	2·514
36·555	16551	−36	$13\bar{3}$	19	2·458
36·745	16717	29	202	12	2·446
37·545	17427	−37	$20\bar{4}$	10	2·396
37·795	17652	27	133	24	2·380
40·120	19799	−16 −23	$22\bar{1}$ 040	12	2·247
40·340	20006	17	041	5	2·236
41·000	20639	−61	221	5	2·201
41·330	20955	33	$22\bar{3}$	7	2·184
42·045	21655	35	222	10	2·149
42·390	21996	8 33	043 135	23	2·132
44·145	23763	−25	044	6	2·051
45·100	24747	13	0010	75	2·010
45·960	25647	−4	$13\bar{7}$	14	1·975
52·720	33174	5	$13\bar{9}$	6	1·736
53·975	34655	−10 −40	150 $24\bar{1}$	6	1·699
55·000	35878	−18	$20\bar{1}0$	12	1·670
55·605	36606	−31	$31\bar{4}$	17	1·653
57·545	38984	−69	313	7	1·602
61·825*	44484	8 12	$33\bar{1}$ 060	40	1·499

$2\theta_{obs}$ in degrees: Cu$K\alpha$ $\lambda = 1{\cdot}5418$ Å
Cu$K\alpha_1$ $\lambda = 1{\cdot}5405$ Å
d = interplanar spacing in Å
$Q = 1/d^2$
$\Delta Q = Q_{calc} - Q_{obs}$
I = relative intensity based on arbitrary linear scale
* = α_1

These values are in accord with those found by other workers from single-crystal data for natural 2M muscovite.

The X-ray powder data for the natural 3T polymorph from Sultan Basin, Washington, described by Axelrod and Grimaldi (1949), is given in Table 5. The parameters of the unit cell were found to be:

$$a = 5{\cdot}203 \pm 0{\cdot}01 \text{ Å}$$

$$c = 29{\cdot}988 \pm 0{\cdot}005 \text{ Å}.$$

The parameters given by Axelrod and Grimaldi are for a three-layer monoclinic cell having $\beta = 90° \pm 10'$.

The densities of synthetic 1M, synthetic 2M, and natural 3T muscovite, calculated from the above unit-cell constants, are, respectively, 2·804, 2·831, 2·821.

Table 5. X-ray powder data for a natural 3T muscovite
(Specimen described by Axelrod and Grimaldi, 1949)

$2\theta_{obs}$	$Q_{obs} \times 10^5$	$\Delta Q \times 10^5$	*hkl*	*I*	*d*
8·870	1006	−5	0003	>100	9·969
17·770	4014	−11	0006	53	4·991
19·765	4956	−30	$10\bar{1}0$	19	4·492
19·905	5026	11	$10\bar{1}1$	19	4·460
22·960	6666	39	$10\bar{1}4$	10	3·873
24·755	7732	−26	$10\bar{1}5$	8	3·596
26·760	9011	−4	0009	>100	3·331
28·705	10341	34	$10\bar{1}7$	10	3·110
31·010	12025	18	$10\bar{1}8$	16	2·884
34·645	14918	−29	$11\bar{2}1$	15	2·589
35·000	15216	7	$11\bar{2}2$	27	2·564
35·935	16013	0	00012	11	2·499
36·565	16560	−3	$11\bar{2}4$	7	2·457
37·730	17593	−35	$11\bar{2}5$	8	2·384
39·990	19675	29	$20\bar{2}0$	5	2·254
40·590	20245	−18	$11\bar{2}7$	4	2·222
41·080	20715	−10	2023	4	2·197
42·310	21918	−23	$11\bar{2}8$	12	2·136
44·035	23650	57	$20\bar{2}6$	3	2·056
45·365	25022	−2	00015	47	1·999
46·160	25859	39	$11\bar{2}10$	7	1·966
48·285	28149	84	$11\bar{2}11$	2	1·885
55·550	36545	28	$11\bar{2}14$	10	1·654
56·165	37289	−27	$21\bar{3}5$	3	1·638
57·065	38392	−7	$21\bar{3}6$	3	1·614
59·605	41564	35	$21\bar{3}8$	2	1·551
60·925	43248	−3	$11\bar{2}16$	6	1·521
61·765	44332	2	$30\bar{3}0$	11	1·502

$2\theta_{obs}$ in degrees: Cu$K\alpha$ $\lambda = 1{\cdot}5418$ Å

d = interplanar spacing in Å

$Q = 1/d^2$

$\Delta Q = Q_{calc} - Q_{obs}$

I = relative intensity based on arbitrary linear scale. Not reliable because of preferred orientations

Natural 1Md and 1M Muscovites

The search for those muscovites based on a one-layer unit cell was guided by the fact that they usually had been obtained experimentally at low temperatures and in runs of short duration. Natural environments of equivalent nature would probably include the sediments, lowgrade metamorphic rocks, secondary alteration zones, and some pegmatite deposits. A brief description of the specimens examined by means of powder X-ray diffraction, and the results obtained, are summarized below. The mixed-layer specimens were also X-rayed, after soaking in ethylene glycol, to verify the presence of montmorillonite deduced from a basal spacing larger than that expected for muscovite.

Sericite. East flank of Mt. Sheridan, Yellowstone Park, Wyoming. No. YP51-230, F. R. Boyd. In altered rhyolite. 1M (with quartz).

Sericite. Germantown, Penn. In Wissahickon schist and granitic gneiss at abandoned quarry on the west bank of the Wissahickon Creek. Considered to be late stage hydrothermal product by Postel and Adelhelm (1944). 2M.

Sericite. Rutherford Mine, Amelia, Virginia. No. 1, water green. Glass (1935). In pegmatite. 1M + 2M.

Sericite. Rutherford Mine, Amelia, Virginia. No. 2, maize yellow. Glass (1935). In pegmatite. 1M + 3T (?).

Sericite. Rutherford Mine, Amelia, Virginia. No. 3, analine lilac. Glass (1935). In pegmatite. 3T.

Sericite. Rutherford Mine, Amelia, Virginia, No. 4, greyish lavender. Glass (1935). In pegmatite. 1M + 3T.

Sericite. Rutherford Mine, Amelia, Virginia. No. 5, chalcedony yellow. Glass (1935). In pegmatite. 2M.

Sericite. Chibougamau, Quebec. Collected by Gilles Allard. In chloritoid-sericite vein with siderite and chlorite. 2M.

Illite. Junction of McIntyre and McRavish townships at the shore of Lake Superior, Ontario. S. A. Tyler. Granules in conglomeratic facies of the Gunflint iron formation. 1M (with quartz and dolomite).

Illite. Fithian, Vermilion Co., Illinois. Purified by R. E. Grim. Pennsylvanian underclay. Mixed-layer 1Md + montmorillonite and 2M.

Illite. Fithian, Vermilion Co., Illinois. Purified by P. Kerr, Pennsylvanian underclay. Mixed-layer 1Md + montmorillonite and 2M.

Illite. Fithian, Vermilion Co., Illinois. Unpurified. Gift of G. T. Faust. 2M + quartz + montmorillonite.

Illite. Ballater, Aberdeenshire, Scotland. Mackenzie, Walker, and Hart (1949). In decomposed granite. 3T + montmorillonite.

Illite. Morris, Illinois. No. 36. Kerr *et al.* (1950b, p. 57). Underclay. Mixed-layer 1Md + montmorillonite, 2M and quartz.

Sarospatakite. Sarospatak, Hungary. Maegdefrau and Hofmann (1938b). Mixed-layer 1M + montmorillonite (10 per cent).

Potash bentonite. Chickamauga Dam, Chatanooga, Tenn. Ross and Hendricks (1945, p. 67). Altered latite. Mixed-layer 1M + montmorillonite.

Potash bentonite. Chattooga Co., Georgia. C. S. Ross. Mixed-layer 1M + montmorillonite.

Potash bentonite. High Bridge, Kentucky. Bradley (1945). Kerr *et al.* (1950a, p. 13). Courtesy of C. S. Ross. Altered volcanic ash. A potash-bearing Ordovician clay. No mica; feldspar + quartz + montmorillonite.

Glimmerartiger Ton. Monte Caslano, Switzerland. Magyar and von Moos (1947). Triassic sediment. Mixed-layer 1Md + montmorillonite.

Muscovite-like kaolin mineral. Franklin, N. C. Ross and Kerr (1948, p. 172–173). Vermicular crystals resembling kaolinite and altered (?) to kaolinite in clay deposit. Similar materials have been referred to as secondary muscovite, sericite, or hydromica: Kaolinite with mica (5 per cent, polymorph not distinguishable).

Secondary mica. Cox Deposit, Hayesville, N.C. Sand and Bates (1952) No. S-122, 31-74 μ fraction consisting of 50 per cent mica and 50 per cent kaolinite. In weathered pegmatite. Kaolinite with mica (10 per cent, polymorph not distinguishable).

Secondary mica. Nat Kidd Prospect, Roseland, Nelson Co., Virginia. No. S-123. Sand and Bates (1952). 31-74 μ fraction consisting of 50 per cent mica and 50 per cent kaolinite. In weathered nelsonite: Mica (50 per cent, polymorph not distinguishable) with feldspar (20 per cent), kaolinite (25 per cent), and quartz (5 per cent).

Secondary mica. Funkhauser Mica Mine, Hartwell, Hart Co., Georgia. No. S-107. Sand and Bates (1952). 8-16 μ fraction consisting of 20 per cent mica and 80 per cent kaolinite. In weathered pegmatite. Mica (40 per cent, polymorph not distinguishable) with kaolinite (40 per cent) and feldspar (20 per cent).

Hydrous mica. Yorkshire, England. Carr, Grimshaw, and Roberts (1953). Flaskes, 2–3 mm square, in fireclay. Believed by them to be diagenic in origin. 2M.

Hydromica. Mineral Joe Mine, Jo Dandy Mining Group, Paradox Valley, Montrose, Colo. No. G27UM, R. M. Garrels. Total water content 9 per cent: mixed-layer 1Md + montmorillonite and 2M.

Pinite. Falun, Sweden. No. 160, H. S. Yoder. Alteration product of cordierite. 1M + 2M (with quartz and kaolinite).

Pinite. Pini Mine, at Aue, near Schneeberg, Saxony, Germany. U.S.N.M. 103809 Alteration product of cordierite in granite. 1M + 2M.

Damourite. Stoneham, Maine. U.S.N.M. 45075. Alteration of topaz. 2M.

Damourite. Hebron, Maine. U.S.N.M. 49179. Alteration of tourmaline. 2M.

Mariposite. Lone Mountain, Esmeralda Co., Nevada. P. W. Racey, through courtesy of W. T. Schaller. 2M + 1M (with quartz).

Mariposite. App Mine, Quartz, California. U.S.N.M. 94494. Dark green. Knopf (1929, p. 38). In ankerite. 1M (with chlorite and quartz).

Gieseckite. Klondike Corundum Workings, Cut No. 3, Raglan township, Renfrew Co., Ontario. Stop II, Locality 1, G. S. A. Field Trip, Hewitt (1953). Green alteration of nepheline gneiss. 1M (with chlorite).

Hydronephelite. American Nepheline Corporation Quarry No. 2, Blue Mountain, Ontario. Hewitt (1953). Pink alternation along joints in nepheline syenite. 1M (with paragonite).

Groppite. Gropptorp, Sweden. U.S.N.M. R4927. In limestone. 1M (with chlorite).

Muscovite. Cape granite, Kloof Quarry, Capetown, South Africa. L. O. Nicolaysen 2M.

Celadonite. Reno, Nevada. HENDRICKS and Ross (1941, p. 685). Vesicular fillings in olivine basalt. 1M.

It is obvious from a cursory examination of the minerals described above that the 1Md and 1M structures are common in nature. In addition, materials having these structures are recorded in the literature, but with one exception not recognized

Table 6. *Published X-ray powder data for* 1*Md and* 1*M muscovites*

Synthetic NOLL (1932)		*Synthetic* GRUNER (1942)		*Sarospatakite* MAEGDEFRAU *and* HOFMANN (1938a)		GRIM's *Illite* MAEGDEFRAU *and* HOFMANN (1938a)		*"Hydro-muscovite"* NAGELSCHMIDT (1937)		*Illite* LEVINSON (1955)	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
		10·09	6	10·09	3	10·15	4	9·98	4	10·1	7
		4·86	2	5·01	2	4·92	2	5·02	4	4·98	5
4·48	5	4·44	7	4·45	5	4·45	5	4·51	3	4·50	7
										4·35	2
										4·10	2
		*3·898	1							*3·85	2
3·70	3	3·649	2	3·64	2	3·67	1/2	3·62	4	3·62	6
3·37	5	3·339	6	3·31	3	3·31	3	3·34	5	3·32	7
3·09	1 ?	3·118	1	3·07	2	3·05	1/2	3·09	4	3·08	6
2·84	5	2·822	2					†2·89	4	*†2·89	4
		2·708	1								
										2·67	3
2·56	9	2·560	6	2·56	5	2·57	5	2·59	5	2·57	8
2·46	4	2·471	2	2·46	1	2·47	1	2·470	3	2·47	3
2·38	1	2·370	2	2·38	2	2·37	2	2·390	4	2·38	5
		2·239	2	2·24	1	2·25	1	2·27	2	2·25	4
								2·18	2		
2·147	4	2·138	2	2·13	2	2·13	1	2·135	4	2·14	5
2·016	6	2·016	1	2·00	1/2	2·00	1	1·994	5	1·99	7
		1·974	1								
1·828	1 ?	1·872	1								
		1·703	1	1·69	1	1·70	1	1·715	1	1·71	2
1·654	7	1·653	2	1·63	1	1·64	2	1·648	4	1·65	5
										1·58	1
1·504	9	1·501	5	1·50	4	1·50	4	1·505	4	1·50	7

* Possibly a 3T spacing.
† Probably the principal dolomite spacing.
Intensity scales independent and relative.

as such; several examples are cited in Table 6. There are many more examples known of materials which contain mixtures of the 1M structure and other polymorphs. Although most of the minerals examined are straightforward

varieties of muscovite with minor variations in composition, there are three mineral groups with require closer examination: illite, hydromica and sericite.

Illite

"The term illite was proposed by Grim, Bray, and Bradley, in 1937, as a general term, not as a specific clay mineral name for the mica-like clay minerals" (Grim, 1953, p. 35). Grim (1953) has further defined the term illite as follows:

1. "shows substantially no expanding-lattice characteristics." (p. 36).

2. "include both trioctahedral and dioctahedral types . . ." (p. 36).

3. "Most of the illite clay minerals so far described are dioctahedral, but some are known that are trioctahedral with unit cells composed of one, two, or three silica-alumina-silica layers." (p. 67).

4. "There is some randomness in the stacking of the layers in the *c* direction . . ." (p. 67).

5. "the size of the illite particles occurring naturally is very small, of the order of 1 to 2 microns or less." (p. 67).

6. "a mica-type clay mineral with a 10-A *c*-axis spacing . . ." (p. 36).

7. "The 10-A diffraction line . . . is often modified into a band which tends to tail off slightly toward the low-angle region as a consequence of the small particle size, variation in the interlayer cation, and occasional slight interlayer hydration." (p. 67).

8. "It is conceivable that all gradations can exist between illite and well-crystallized muscovites and biotites on the one hand and montmorillonite on the other hand." (pp. 68-69).

9. "the interlayer balancing cations are not exchangeable." (p. 68).

10. "Many clays are known which seem to be gradational between illite and montmorillonite, but which are actually composed of interlayered mixtures of true illite and montmorillonite . . ." (p. 69).

11. The composition of illite has been presented by Grim and his co-workers in several different forms, which are interpreted to be:

(a) $2K_2O \cdot 3MO \cdot 8R_2O_3 \cdot 24SiO_2 \cdot 12H_2O$ (1937, p. 823),

(b) $K_y(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)(Si_{8-y} \cdot Al_y)O_{20}(OH)_4$, where $y = 1-1{\cdot}5$ (1939, p. 141),

(c) $K_{1{\cdot}33}(R_4^{+3}, M_6^{+2})(Si_{6{\cdot}67}Al_{1{\cdot}33})O_{20}(OH)_4$ (deduced from example in 1953, p. 67).

12. "The illites differ from muscovite . . . by having a water loss below 100°C and a more abrupt loss of much of the OH lattice water between about 300° and 600°C. . . . the clay-mineral micas differ from the well-crystallized micas in having some interlayer water . . ." (p. 234–235).

One may conclude from these formulae and statements that Grim *et al.* believe the illites to contain more SiO_2 and H_2O and less K_2O than muscovite. Formula (a) can be written in the structural form of a mica having one interlayer of water:

(a) $K_{0{\cdot}66}(M_{0{\cdot}50}^{+2}\ Al_{2{\cdot}66})Si_4O_{10}(OH)_2 \cdot H_2O$.

It is obvious that the aluminium is in excess of that required for a dioctahedral mica. A mica having one interlayer of water could not have a *c*-spacing of 10 Å. Aside from these difficulties, it would appear as though the illites having this

general formula would be close to the join Al-celadonite[4]—montmorillonite, $KAlMgSi_4O_{10}(OH)_2$—$Al_2Si_4O_{10}(OH)_4$. Note should be made of the fact that the charge balanced by the potassium is situated in the octahedral layer. Formula (b) suggests that the illites lie on the join montmorillonite-muscovite, and represent a limited series of solid solutions near montmorillonite. The charge balanced by the potassium in this case is situated in the tetrahedral layer. Formula (c) also represents the same join as formula (b); however, the limited solid solution is about muscovite and extends one-third of the way towards montmorillonite. It will be assumed that formula (c) represents the latest view of GRIM. On this basis the writers wish to comment on the salient points of definition quoted above.

With regard to quotations 4, 6, and 9, the writers conclude that illite is essentially a 1Md muscovite. On the other hand, GRIM infers in quotation 3 and elsewhere that all the polymorphs may be found in the illites.[5] In his examples of X-ray powder patterns only 2M structures are represented in 1937 (pp. 821–822), and in 1953 (p. 94) he gives examples of the 3T (Ballater) and 2M (Gilead) structures for the dioctahedral types. Oddly enough, the "sericite-like mineral" from GRIM X-rayed by MAEGDEFRAU and HOFMANN (1938) has a 1M structure (see Table 6). From the mineral list above it is clear that materials called illite may have any or all of the polymorphs (see also LEVINSON, 1955). This conclusion contradicts quotation 6.

Quotations 7, 8, and 10 indicate that most illites are in fact mixed-layer structures, and cannot be regarded as solid solutions of the type defined by formula (c). The characteristics of the "10-A diffraction line" which GRIM describes are those of Fig. 1(f), a complex mixed-layer structure. Such structures can be regarded only as being composed of two or more phases. This conclusion has apparently been reached by KERR *et al.* (1950a, p. 13) and JACKSON *et al.* (1952, p. 5), as well as others.

There is no doubt that a very limited amount of solid solution of the type indicated by formula (c) can take place, i.e., $Si \rightarrow KAl$. However, it is most unlikely that such limited substitution would weaken the bonding between contiguous silica sheets to permit interlayer water. The writers are of the opinion that the base exchange capacity and high water content of some of the described illites are due to the montmorillonite member of a mixed-layer structure. Owing to the small size of the illite particles (quotation 5) it is likely that some potassium ions are on an accessible surface and may be base exchanged. As is shown below, grinding less than thirty hours reduces the size of mica below the unit-cell size, and extensive base exchange may be expected. GRIM and BRAY (1936) have demonstrated that the base exchange capacities of illite increase as the particle size decreases in the range 1 μ to less than 0·06 μ.

In quotation 8 GRIM infers that illities are less well crystallized than [2M]

[4] The term Al-celadonite is defined as the composition $KMgAlSi_4O_{10}(OH)_2$, previously referred to as leucophyllite by SCHALLER (1950). The analysis of leucophyllite appears to have been made on impure material (HEINRICH *et al.*, 1953). The Al-celadonite is dioctahedral and is an analogue of celadonite, $KMgFeSi_4O_{10}(OH)_2$, the principal component of the glauconites (HENDRICKS and ROSS, 1941).

[5] Some workers have gained the wrong impression, from the first part of quotation 3, that by the word "dioctahedral" GRIM meant that most illites have the 2M structure, the only dioctahedral structure known to him at that time.

muscovite. It is not clear whether he means the peaks on the X-ray pattern of illite are broad owing to fine grain size, or that some peaks tail off to *higher* angles owing to disorder. The writers have not observed a 2M muscovite which exhibits either of these diffraction phenomena. Only the 1M polymorphs have exhibited peak broadening, presumably because of the fine grain size. (Only those patterns in which the *hkl*'s are absent have been called disordered by definition.)

It is concluded, therefore, that the term *illite* should be used only as a field term, as Grim *et al.* originally proposed. When identification is made of the material or materials, the polymorph of the mica should be specified, and note made of the clay mineral with which it may have formed mixed layers. Proof has yet to be obtained that the materials now called illite are not all mixed-layer structures. The alleged solid solution between muscovite and montmorillonite could be demonstrated by the existence of an analyzed specimen having a 1M structure and an X-ray pattern of sharp, symmetrical peaks. The *c*-spacing should lie between that of montmorillonite and muscovite, and no subsidiary reflections would be permissible. In addition, the specimen should exhibit no expansion characteristics or base exchange properties. The "true illite" referred to by Grim in quotation 10 is specifically a polymorph of muscovite.

Hydromica

The first use of the term *hydromica* appears to be that of Galpin (1912), and the terms hydrous mica[6] and hydromuscovite are considered to refer to the same type of material. The original material was not available for study; however, C. S. Ross supplied the writers with similar materials. Only kaolinite was recognized in the X-ray pattern, although two distinct phases are clearly seen under the microscope. Nacrite or dickite may be the second phase. No attempts were made to separate the two intimately intergrown phases.

Hydromica has been grouped with the illites; however, a different type of substitution is inferred by Ganguly (1951), and by Brown and Norrish (1952). These workers independently proposed that H_3O^+, the oxonium ion, which has a radius approximately that of potassium, substitutes for K^+. In this way the high H_2O+ and low K_2O content were accounted for in some materials. Brown and Norrish obtained good agreement with the ideal mica formula by distributing the atoms obtained by analysis in the following way:

$$(Ca,Na,K,H_3O)_2(Al,Ti,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4.$$

In this scheme it was assumed that the analyses of the alkalies and water were accurate and precise. Support for the existence of the H_3O^+ ion in the layered structures was presented earlier by Foster (1951), when she demonstrated by analysis that H^+ was part of the exchangeable ions in two montmorillonites.

Foster also showed that Mg^{++} was present in significant amounts among the

[6] Hendricks and Alexander (1939, p. 264) define hydrous mica as follows:

$$KAl_2(AlSi_3)O_{10}(OH)_2 \cdot xH_2O.$$

The existence of a muscovite with interlayer water has not as yet been demonstrated. Because of the strong bonding forces, it is unlikely that a muscovite of normal potassium and silica content would contain water between the mica units.

exchangeable ions. When the Mg was properly partitioned on the basis of cation-exchange measurements, good agreement was obtained with the ideal formula, with the exception of water content. It is important to note that, in partitioning the MgO content, the Mg assigned to the exchangeable ions was treated as a univalent ion (FOSTER, 1951, p. 728). BOWER and TRUOG (1940) had arrived at a similar treatment on the basis of results obtained on cation-exchange capacities, using cations of different valency.[7] The magnesium might be considered as present as a complex such as $Mg(OH)^+$, occupying a position between the structural units in the manner pictured by MARSHALL (1949, p. 59). It is the opinion of the writers that exchangeable cations cannot occupy the structural position of potassium in the *ideal* structure. There appears to be little doubt that exchangeable ions are held by virtue of an unbalanced charge originating within the structure; however, some cations may be exchangeable because they occupy sites at the surface of a broken particle. A distinction must be made between an unbalanced charge originating by replacement of ions of different charge within the muscovite structure, and a charge arising from broken bonds which is wholly a surface phenomenon.

Sericite

Sericite is a field term used to describe any fine-grained white mica.[8] Materials called sericite, having the muscovite composition, appear to exhibit all the known polymorphs of muscovite, and there is no reason to believe that they are basically different from muscovite. SCHALLER (1950) has called attention to materials which he refers to as " high-silica sericites." The only permissible substitution leading to the high silica content which can operate within the dioctahedral structure is $M^{+2}Si \rightarrow 2R^{+3}$, where M^{+2} is usually Mg^{+2}, and R^{+3} is Fe^{+3} as in celadonite. The charge to be balanced by the potassium originates in the octahedral layer (see FOSTER, 1953). The materials cited by SCHALLER as members of the join muscovite —Al-celadonite are also low in K_2O and high in H_2O+. Although the scheme of SCHALLER accounts for the high silica and the magnesium content, it does not explain the low K_2O and high H_2O+. This suggests that the "high-silica sericites" may in addition exhibit the type of solid solution alluded to by GRIM for the join muscovite—montmorillonite, another "high-silica" series.

The three substitution schemes deduced above for the illites, hydromicas, and sericites, are, respectively, as follows:

(a) $Si \rightarrow KAl$
(b) $H_3O \rightarrow K$
(c) $MgSi \rightarrow 2Al$.

There is the possibility, in addition, of limited solid solution with the trioctahedral micas. For example, low K_2O may be achieved by the following scheme:

(d) $2Mg \rightarrow KAl$.

Here the normal silica content would be retained.

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[7] FOSTER (1951, p. 722) appears to have inadvertently misstated her own conclusions with regard to the treatment of magnesium as a univalent ion or complex. She is in agreement with BOWER and TRUOG (FOSTER, personal communication).

[8] The white micas include muscovite and paragonite. The paragonite problem will be considered fully in a paper by EUGSTER and YODER (abstr., 1954a; review, 1954b).

The purpose of these remarks is to emphasize the fact that all four substitution schemes can take place in the muscovite structure. Mixed-layer materials have added considerable confusion to these problems, and every effort should be made to secure homogeneous, single-phase material for future study.

In view of the slightly low K_2O and high H_2O+ contents of some synthetic muscovites prepared in open capsules (e.g., 9·7 and 6·35 per cent, respectively), it appears as though some substitution of the type (b) has taken place. If K_2O was leached, a sixfold loss of SiO_2 must also have taken place, according to Morey's experiments. It is likely, therefore, that some of the synthetic muscovites lie close to the ideal muscovite on the muscovite—oxonium muscovite join, rather than on the muscovite—montmorillonite join.

On the assumption that the substitution schemes (a), (b), and (c) are the major replacement mechanisms in the micas, it is possible to plot the composition of such materials in the system muscovite—Al-celadonite—pyrophyllite, and their iron analogues. A point in such a system may be specified uniquely by considering only two features of a chemical analysis:

(1) The tetrahedrally co-ordinated atoms required to satisfy the silicon position.

(2) The sum of the octahedrally co-ordinated ions having a valence of 3.

The advantage of these two features is that they do not involve the problems of either the partition of the $M^{+2}O$ group or the H_2O+. The alkalies, H_3O^+, exchangeable ions, and $M^{+2}O$, are grouped and should equal the third co-ordinate in the ternary system. The results of such a plot are given in Fig. 11. The analyses are from the following sources:

Celadonites Glauconites	Hendricks and Ross (1941)
Montmorillonites	Ross and Hendricks (1945) Foster (1953)
Illites	Foster (1955, unpublished data)
Pyrophyllites Nontronites	Ross and Hendricks (1945)
High-silica sericites	Schaller (1950).

Mixed-layer structures and mixtures were included in the plot, except where it was clear that kaolinite or some other phase, the composition of which cannot be represented in the plane, was present. Only areas representing a large number of analyses have been outlined.

It is concluded from this crude study of the analyses of these materials that they are well represented in the chosen system by the proposed substitution schemes. There is no doubt that the wide extent of the field of each mineral group is partly due to mixtures or mixed-layer assemblages. Their extent should not be interpreted as wholly due to solid solution. Synthesis studies of this system may aid considerably in defining the limits of the proposed substitutions.

Effects of Grinding

It is well known that grinding affects the structure of muscovite. A natural 2M muscovite from Spruce Pine, N.C., was filed to −325 mesh and ground dry in a motor-driven agate mortar for thirty-six hours. Samples were taken at two-hour intervals, and powder X-ray diffraction records made of a portion of the total product. The peak heights of two representative reflections (002 and 114) were measured relative to the 002-peak in filed material. The extent of the structural

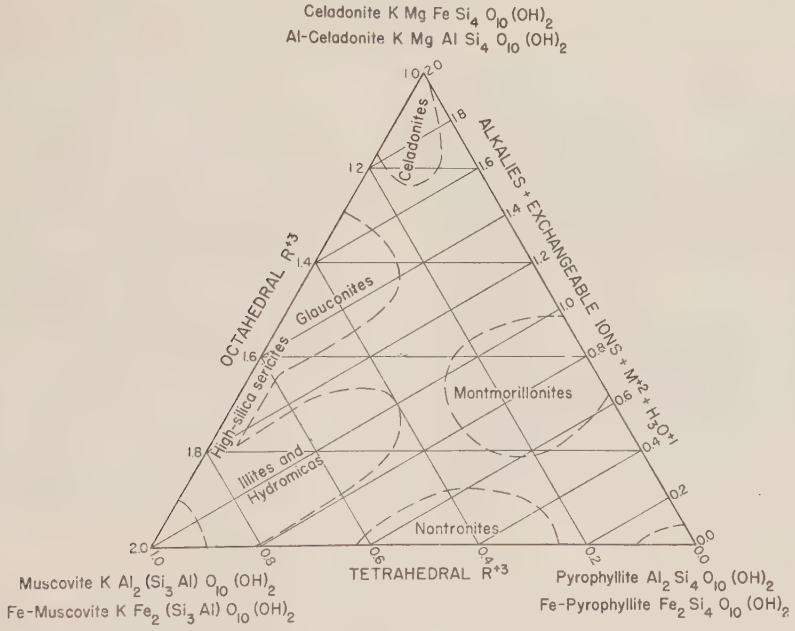


Fig. 11. Plot of tetrahedral R^{+3} and octahedral R^{+3} in atom proportions of dioctahedral micas and related minerals.

damage may be seen from the data in Fig. 12. No peaks were apparent in the X-ray pattern after thirty hours' grinding.

In Fig. 13a is given the electron-micrograph of the product after thirty hours' grinding in the agate mortar. The size and shape of the particles have been altered considerably. The transmission selected-area electron-diffraction pattern obtained from the central portion of the aggregate in Fig. 13a is given in Fig. 13b. The few remaining diffraction spots suggest that the degree of crystallinity has been measurably reduced as a result of prolonged attrition. It is to be recalled that the theoretical wavelength of a 50-kV electron beam is approximately 0·056 Å. It is likely that the periodicity of the muscovite unit cell has been completely obliterated after thirty-six hours' grinding.

The effect of grinding on muscovite has been studied previously in detail by Mackenzie and Milne (1953). They concluded that "more or less complete breakdown of the muscovite structure is induced by about eight to nine hours' grinding, and that after this recrystallization takes place. . . . The product of recrystallization after prolonged grinding appears . . . to be a form of illite. . . ."

It is desirable to analyse the arguments presented by them with regard to the alleged recrystallization phenomena.

(a) The cation-exchange data indicate no change after eight hours' grinding and therefore indicate no change of phase, i.e., recrystallization of a previously existing phase.

(b) The published X-ray diffraction pattern of the original material indicates mostly 2M and some 1M muscovite. After eight hours' grinding the published pattern is that of a 2M muscovite with greatly reduced intensities; no change in the sharpness of the peaks is apparent in their published photograph. After twenty-four hours' grinding the pattern consists of a mixture of 1M muscovite + 2M muscovite. It is a common experience to obtain incomplete comminution of grains at the periphery of a motor-driven agate mortar, and therefore it is possible that

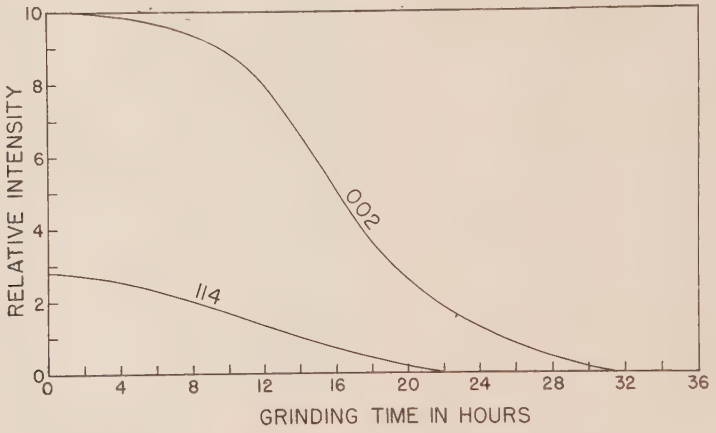
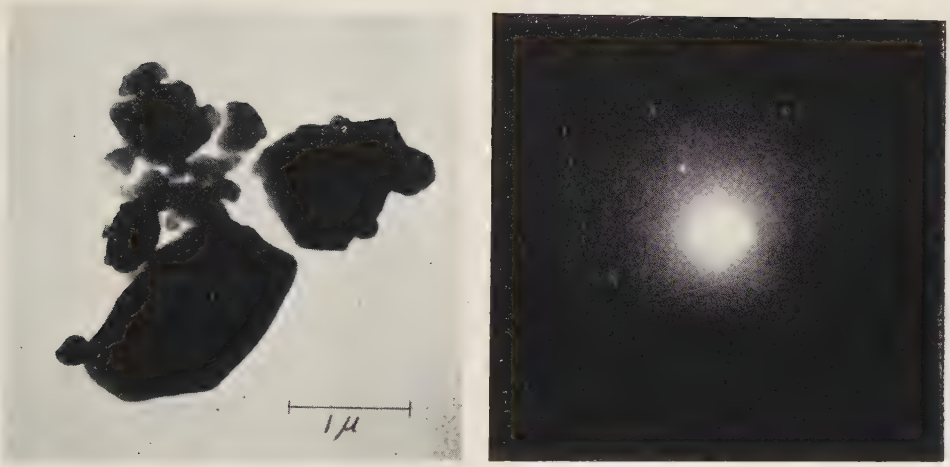


Fig. 12. Relative intensity of the 002 and 114 reflections of natural muscovite ground up to thirty-six hours.

Mackenzie and Milne sampled this region. They specifically state that only the --200-mesh portion was studied; i.e., inefficient grinding was obviously observed by them at each stage of grinding! The reappearance of the original 1M + 2M muscovites in the material that was ground for twenty-four hours is therefore attributed to incomplete grinding, and not to resynthesis on grinding. The reversal of the intensities of the 1M and 2M polymorphs may be the result of inhomogeneities in the sample, or preferred orientation in the sample preparation. Further difficulty is involved in the fact that Mackenzie and Milne compared their material that was ground for twenty-four hours to the Ballater illite, which is now believed to be a 3T muscovite, and the hydromuscovite of Ogofau, Wales, which is a 1M muscovite.

(c) The differential thermal pattern of the original material shows no peaks, and is not representative of those of muscovites published by other workers. The pattern of the material that was ground for twenty-four hours exhibits the adsorbed water peak at about 100°C, characteristic of almost any very finely ground material, and the peaks at about 1000°C are those usually assigned to normal 2M muscovite. The principal DTA peaks of illite given by Grim and Bradley (1948) are missing.

(d) The chemical analyses appear to be suspect. The material that was ground for twenty-four hours is believed by them to contain more Al_2O_3 and less SiO_2 than



(a) (b)

FIG. 13. (a) Electron-micrograph of Spruce Pine, N.C. 2M muscovite ground dry for thirty hours in an agate mortar.

(b) Transmission-selected area-electron-diffraction pattern obtained from central portion of aggregates in (a).

the original material. However, it is noted that the total $Al_2O_3 + SiO_2$ remains the same. It is a common difficulty in chemical analysis, particularly in microtechniques, to separate completely Al_2O_3 and SiO_2 (Fairbairn *et al.*, 1951).

On first inspection, it appeared as though support for the conclusion of Mackenzie and Milne was to be found in the work of Grim and Bradley (1948). They heated illite at 600°C and 800°C for one hour each, and then allowed the material to sit in the atmosphere for varying periods of time. The DTA curves of the materials left standing indicated to them that the dehydrated illite had picked up both adsorbed water and (OH) water. Unfortunately, they failed to take DTA records of the material immediately after heating, so there is no evidence that all the water was driven out. The work of Roy (1949) indicates that less than 20 per cent of the H_2O+ content of muscovite is removed by heating at 600°C for one hour. The DTA data of Grim and Bradley do show, however, that the fine-grained material adsorbed water on standing.

It is concluded, on the basis of the new grinding data presented above, and the hydrothermal studies, that grinding at room temperature would not bring about either the growth of 1M muscovite or, even more unlikely, the recrystallization of 2M muscovite.

Thermodynamic Considerations

The slow rate of reaction prohibits the determination of the lower-pressure and temperature-equilibrium conditions of the stability curve for muscovite. That portion of the curve may be calculated, using the data obtained at higher pressures and temperatures from known thermodynamic relations.

The breakdown of a hydrous mineral, A, may be generalized as follows:

$$A \rightarrow B + nH_2O$$

where A and B are solids. The equilibrium constant based on partial pressures, K'_P, for such a reaction is

$$K'_P = \frac{P_B \cdot P^n_{H_2O}}{P_A}.$$

From empirical considerations Guldberg and Waage concluded that, whenever a solid is involved in an equilibrium, its activity should be regarded as constant. For this reason the equilibrium constant need not contain any terms for compounds present as solid at equilibrium. The equilibrium constant for a hydrous mineral decomposition is, then,

$$K_P = P^n_{H_2O}.$$

Note that K_P differs from K'_P by the ratio P_B/P_A, which is assumed to be constant.

The integrated van't Hoff relation is

$$\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 \cdot T_2}\right) \text{ or,}$$

$$\ln K_P = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + C,$$

where ΔH is the change of enthalpy, R the gas constant, T the temperature, and C a constant of intregation. Since $K_P = P^n_{H_2O}$, the van't Hoff relation reduces to the integrated Clausius-Clapeyron equation

$$n \ln P_{H_2O} = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + C, \text{ or,}$$

$$n \log P_{H_2O} = -\frac{\Delta H}{2{\cdot}303R}\left(\frac{1}{T}\right) + C.$$

The assumptions made in the integration are:

(1) The enthalpy is not a function of the temperature.

(2) The specific volume of the solids is negligible.

(3) The volume of the vapour can be expressed by the ideal gas law, $PV = RT$.

These assumptions are only crude approximations. The enthalpy is obviously not independent of temperature, according to the relation:

$$d\Delta H = \Delta C_p \, dT.$$

The specific volume of the solids is not negligible compared to that of the gas, especially at high pressures. Water is a non-ideal gas, and its behaviour cannot be represented by the perfect gas law. At 1500 bars and 690°C, for example, PV_{obs}/PV_{ideal} is 0·81. However, the errors introduced by these approximations tend to cancel each other, according to Steiner (1941, p. 199), and the integrated equation fits the experimental data in a large number of cases. (It should be noted also that ΔH obtained in this way is the result of an intregation which tends to average the values over the experimental range.) The approximate enthalpy may be determined, therefore, from the integrated Clausius-Clapeyron equation by a plot of log $P^n_{H_2O}$ vs. $1/T$. The slope of the resulting curve is $-\Delta H/2{\cdot}303R$. With ΔH determined, other equilibrium values of P and T may be calculated.

The following experimental values were used in computing the lower portion of the muscovite P-T curve:

Pressure, atm.	*Temperature,* °K
(340)	(898)
680	918
1020	938
1530	963
2040	988

One point which may not represent equilibrium is indicated by parentheses. The plot of $1/T$ vs. log P_{H_2O} is given in Fig. 14. It appears as though ΔH is constant in the lower-pressure and temperature region, and the assumptions may be considered as valid in that region. (At the highest pressure investigated, the deviation from linearity is only 8°, and the deviation at the lowest pressure is only 15°.) The enthalpy of reaction obtained in this fashion is approximately 31·6 kcal/mol. The lower portion of the muscovite curve computed using this value for the enthalpy is given in Fig. 6. The equilibrium temperature at 1 atm pressure is approximately 395°C.

It is of interest to compare the ΔH obtained from the log P vs. $1/T$ plot of some of the hydrous minerals. In Fig. 15 are given the curves obtained by experiment for the decomposition of phlogopite (Yoder and Eugster, 1954), clinochlore (Yoder, 1952), analcite (Yoder, 1954), paragonite (Eugster and Yoder, 1954a), and muscovite. Since the curves of phlogopite, analcite, and clinochlore are approximately parallel, the decomposition reactions have therefore about the same ΔH. This ΔH is approximately that of the heat of dissociation of liquid water at 25°C. The ΔH for the decomposition reactions for muscovite and paragonite are of the same order of magnitude, and very close to half of that of the former three

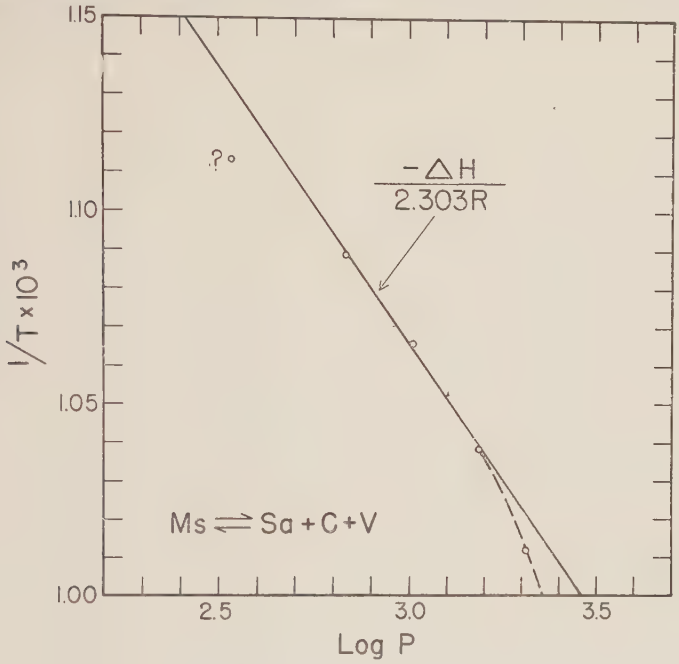


Fig. 14. Plot of $1/T$ vs. log P from data determined experimentally for the reaction Ms $\rightleftharpoons$ Sa + C + V. One point indicated with a question mark is believed not to represent an equilibrium condition.

reactions. It is believed that these similarities are fortuitous, and that the enthalpy of decomposition would be expected to be different for different hydrous minerals.

An alternative method of calculating ΔH for the muscovite breakdown reaction has been suggested by G. J. F. MacDonald (1955, personal communication). Since

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V},$$

and,

$$\Delta H = T\Delta S$$

then the enthalpy of the reaction is given by

$$\Delta H = T \cdot \Delta V \cdot \frac{dP}{dT}.$$

The dP/dT is approximately constant between 1000 and 2000 bars, and is about 20 bars/deg. At 1500 bars the equilibrium temperature is 963°K. The volume change can be estimated from the densities of the solids at standard conditions and the measured volume of water at 690°C and 1500 bars (Kennedy, 1950, p. 555), and is equal to 30·8 cc/mol. The ΔH for the muscovite breakdown reaction at 963°K and 1500 bars is therefore 14·2 kcal/mol. This value of ΔH (963°K and 1500 bars) involves only the assumption that the volumes of the solids were independent of pressure and temperature. It is necessary to know the heat capacities of all the phases to obtain ΔH_{298}. The large discrepancy between the values of

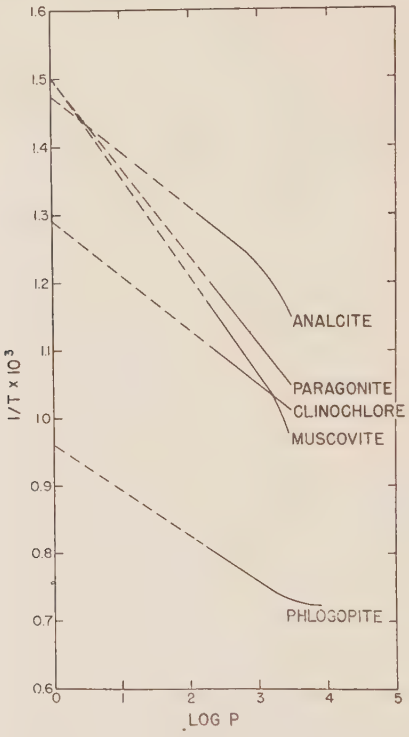


Fig. 15. Comparison of $1/T$ vs. log P plot of various hydrous mineral breakdown curves.

ΔH obtained by the two different methods cannot be accounted for by the heat-capacity terms, since the ΔH found by the first method is assumed to be constant over most of the experimental range. The error introduced by the assumption in the second case is probably negligible, and therefore the ΔH at 963°K and 1500 bars is considered to be the more reliable. On the other hand, the log P vs. $1/T$ plot does yield a straight line, and it would appear as though the assumptions made in the first case are also valid.

The heat of formation, ΔH_{298}, of muscovite may be estimated, since ΔH_{Ms} is given by:

$$\Delta H_{\mathrm{Ms}} = \Delta H_{\mathrm{Sa}} + \Delta H_{\mathrm{C}} + \Delta H_{\mathrm{V}} - \Delta H_{\mathrm{reaction}}.$$

The ΔH of formation from oxides of sanidine, corundum, and water, are, respectively, as follows:

$$1/2\ K_2O + 1/2\ Al_2O_3 + 3SiO_2 \rightarrow \text{sanidine}\ \Delta H_{298} \approx -56{\cdot}4\ \text{kcal/mol}^{(9)}$$

$$Al_2O_3 \rightarrow \text{corundum}\ \Delta H_{298} = 0$$

$$H_2O\ (\text{water}) \rightarrow \text{vapour}\ \Delta H_{298} = \Delta H_{\text{evaporate}} \approx 10{\cdot}5\ \text{kcal/mol.}^{(10)}$$

On the basis of the plot of $1/T$ vs. log P it was shown that the ΔH_{298} for the reaction muscovite $\rightarrow$ sandine + corundum + vapour is about 31·6 kcal/mol. The ΔH_{298} of formation for muscovite from oxides on this basis is, therefore, approximately −77·5 kcal/mol.

Muscovite + Quartz Reaction

One of the most critical reactions in metamorphic petrology is that of muscovite and quartz (see section below on geological application). Although the conditions of the breakdown of muscovite under water pressures equal to the total pressure clearly mark the upper possible limit of such a reaction, knowledge of the exact conditions would be of great value. The preliminary experiments recorded in Table 7 were aimed at fixing the equilibrium condition of the reaction:

$$\text{Muscovite} + \text{quartz} \rightleftharpoons \text{potash feldspar} + \text{sillimanite} + \text{vapour.}$$

The data given in Table 7a were obtained using an initial charge composed of the Zettlitz kaolinite, synthetic orthorhombic $KAlSiO_4$, and silica glass. Muscovite appears to grow as high as 650°C at 15,000 p.s.i. water pressure, and 675°C at 30,000 p.s.i. It is not likely that the muscovite would grow metastably at these temperatures and pressures (even though it is still within its own stability field), since its speed of growth is considerably less than that of sanidine, mullite,[11] or quartz. The muscovite that grew in equilibrium with quartz in these runs has a significantly larger 2θ angle for the 060 reflection in X-ray powder patterns than that for pure synthetic or natural muscovite. The quality of the reflections did not permit a similar comparison with an $00l$ reflection.

The conditions of the reaction were tested using a mixture of natural orthoclase (No. A: Spencer, 1937) and natural sillimanite from the Benson Mines, N.Y. Since quartz was not observed in the critical runs (Table 7b), presumably due to leaching of SiO_2 from the open capsules, the experiments are not applicable.

It would appear, on the basis of these preliminary experiments, that the univariant equilibrium curve representing the muscovite + quartz reaction lies at a maximum only 15 degrees below that of the muscovite breakdown curve. The

(9) Estimated from heats of solution of iron-bearing orthoclase (Kracek, 1953).

(10) Based on heat of vaporization at 25° C = 10·52 kcal/mol (Kelley, 1949). The hydroxyl bond lengths in ice and water are, respectively, 2·76 Å (Barnes, 1929) and 2·90 Å (Morgan and Warren, 1938). The hydroxyl bond lengths for most compounds containing OH are between 2·7 and 2·8. For this reason it is believed that the rupture of OH bonds in the breakdown of muscovite is analogous thermodynamically to the sublimation of ice.

(11) It is not possible to distinguish between mullite and sillimanite in complex mixtures by X-ray powder patterns. Where it has been possible to distinguish the phases in previous studies, mullite was obtained.

Table 7. Hydrothermal data on muscovite—quartz join

Temp. °C.	*Pressure* $\times 10^{-3}$ *p.s.i.*	*Time hours*	*Products*
	(a) Ka + O—K + SiO_2 (glass) + H_2O		
*200	15	4120	Ka + Ms (?) + Q (?)
*350	15	1460	1Md-Ms + Q (?)
*350	15	2208	1Md-Ms + Q + Sa
*500	15	144	1M-Ms + Q + Sa
610	15	168	1M-Ms + Q + Sa
625	15	24	Sa + Q + 1M-Ms
650	15	18	Sa + Mu + Ms + Q (?)
650	15	25	1Md-Ms + Q + Sa
650	15	183	Sa + Ms + Mu (?) + Q (?)
*675	15	236	Sa + Mu + Q
700	15	188	Sa + Mu + Q
*400	30	1776	1Md-Ms + Q + Sa
*500	30	170	1M-Ms + Q + Sa
*500	30	715	2M-Ms + 1M-Ms + Q + Sa
*600	30	720	2M-Ms + 1M-Ms + Q
*600	30	744	2M-Ms + Q
*650	30	160	2M-Ms + Q
*700	30	189	Sa + Mu + Q
*725	30	188	Sa + Mu + Q
	(b) Sa + Sil + H_2O		
350	15	1460	Ms + Sa + Q
600	15	160	Sa + Sil
600	30	503	2M-Ms + 1M-Ms + Q (?)
650	30	184	Sa + Sil
650	30	500	Sa + Sil + Lc + Ms
700	30	528	Sa + Sil

difference in the conditions of the two curves essentially represents the energy involved in the reaction:

(a) $$3C + 2Q = Mu.$$

An estimate of the ΔH of this reaction can be obtained from

(b) $$3Ms + 4Q = 3Sa + 2Mu + 6V \text{ and}$$

(c) $$Ms = Sa + 2C + 2V,$$

since $$2\Delta H_{(a)} = \Delta H_{(b)} - 3\Delta H_{(c)}.$$

The $\Delta H_{(b)}$ can be obtained by the second method presented in the thermodynamics section, $\Delta H = T\Delta V \frac{dT}{dP}$, using $T = 948°K$, $\Delta V = 108{\cdot}8$ cc/mol, $\frac{dT}{dP} = 20°/1000$ bars. The ΔH of the muscovite + quartz reaction at 1500 bars and 675°C is therefore 48·7 kcal/mol. The heat of formation of mullite from its oxides is, then, −3·0 kcal/mol at 1500 bars and about 675°C. This value, although relatively

insensitive to changes in T and ΔV, is of the order of magnitude predicted by Ramberg (1955, personal communication) and by MacDonald (1955, personal communication). For this reason, it is believed that the preliminary experiments well define the conditions of the muscovite + quartz reaction.

Fluoromuscovite

The average fluorine content of some sixty specimens of natural muscovite for which fluorine was analyzed is 0·58 per cent. The largest amount of fluorine reported in a modern analysis of muscovite is 1·28 per cent (Lokka, 1943, p. 6). It was believed that these small amounts of fluorine would affect the stability range of muscovite, and attempts were made, therefore, to synthesize a fluoromuscovite and determine its upper stability range.

Table 8. *Results of experiments on the fluoromuscovite composition*

Temp. °C	*Pressure* $\times 10^3$ *p.s.i.*	*Time hours*	*Products*
*700	15	181	Sa + To + ?
*725	15	182	Sa + To + ?
*750	15	182	Sa + To + ?
*775	15	163	Sa + To + ?
*850	15	160	To + ?
*400	30	1	No reaction
500	30	408	Sa + To + ?
*500	30	1	F-Ms + Sa + To
600	30	405	Sa + To + ?
*600	30	1	Sa + To + F-Ms
*700	30	1	Sa + To + ?
†710	30	188	Sa + To + ?

† Plus H_2O.

The mix consisted of silica glass + γ-Al_2O_3 + K_2SiF_6 in the requisite proportions. In the attempted production of fluoromuscovite at elevated pressures, the charges turned grey to black, and the products identified were usually sanidine + topaz, a common assemblage in the tin-bearing pegmatites (Table 8). These synthetic products presumably grew metastably, at least at the lower temperatures, in the same manner as sanidine and corundum grew from some mixtures in the region where hydroxyl-bearing muscovite was stable. Fluoromuscovite was obtained in only two runs which were of one hour's duration. The failure to obtain fluoromuscovite in longer runs cannot be accounted for at present.

The synthesis of fluoromuscovite was achieved in 1888 by Doelter, using various fluorosilicate melts. Baur (1911) made "muscovite", identified optically by Becke, at 450°C in a bomb containing water, and obtained in addition pyrophyllite and K_2SiF_6. The fluorine in Baur's experiments is believed by Schlaepfer and Niggli (1914) to have been present as SiF_4 in the initial materials as a result of the incomplete treatment of the silica. It is not known whether the

"muscovite" produced contains OH, F, or both. Eitel (1952) has reported the reaction in the solid state of fluorides at 600°C and 700°C to form, in part, a fluoromuscovite. The work was carried out at the Electrotechnical Laboratory of the U.S. Bureau of Mines, Norris, Tennessee. Through the courtesy of R. A. Hatch, two samples of their products were obtained. Both were synthesized from a mixture of K_2SiF_6 and calcined Putnam clay ($Al_2O_3 \cdot 2SiO_2$) in the proportions of 1 : 3, which was heated in a tightly covered platinum crucible in air at 600° ± 20°C. One sample was held for twenty-four hours, and the other for 192 hours. On the basis of X-ray powder patterns taken by the present writers, the 24-hour sample consisted of 1M-fluoromuscovite (50 per cent) + topaz (30 per cent) + sanidine (20 per cent); and the 192-hour sample of sanidine (70 per cent) + topaz (20 per cent) + 1M-fluoromuscovite (10 per cent). There appears to be no discernible difference in the X-ray patterns of a 1M-muscovite and a 1M-fluoromuscovite. Because of the progressive decrease in amount of fluoromuscovite and the increase in the amount of sanidine, Eitel and his co-workers concluded that fluoromuscovite forms metastably at 600°C in air.

Further study will be required to fix the stability field of fluoromuscovite.

Geological Application

Granites

Muscovite is a common constituent of granites, while biotite is almost universally present, hornblende less common, and pyroxene rare. The muscovite-bearing granites are usually those in which two feldspars, a potash feldspar and a plagioclase are present. Muscovite is absent in those granites in which only one feldspar is present (Chayes, 1955, unpublished data).[12] In New England those granites unusually rich in muscovite tend to be rich in quartz (Chayes, 1952, p. 217). The largest amount of modal muscovite observed by Chayes in a single specimen of granite is 12·2 per cent; much of the muscovite was confined within the plagioclase. There appears to be no consistent interrelation between the amounts of biotite and muscovite in the granites examined by Chayes.

In most muscovite-bearing granites, the muscovite is observed as interstitial flakes as well as dispersed within feldspar. These relations are often interpreted as indicating two generations of muscovite, the earlier formed during the crystallization of the granite, and the later, the so-called sericites, as a subsequent alteration. The relationship of the breakdown curve of muscovite to the minimum melting curve of granite of Tuttle and Bowen (1953), given in Fig. 16, is of particular interest with regard to these observations. Above approximately 1500 atm it is possible for muscovite to form on the liquidus surface of the "granite" system. Below that pressure muscovite can form only in the solid state.

It is possible, therefore, that the interstitial flakes of muscovite in a granite may have formed in equilibrium with a liquid at pressures above 1500 atm, or in the solid state at any pressure or temperature below the stability curve of muscovite. The minute flakes usually dispersed within the feldspars were probably formed

[12] One-feldspar granite is defined by Chayes (personal communication, 1955) as a granite in which only one feldspar is a major constituent. If the feldspar is potassic, it may contain exsolved plagioclase; however, it is assumed that at the time of formation these formed a single phase.

either in the solid state by reaction of the potash feldspar with an aluminium-rich mineral (i.e., sillimanite, cordierite, garnet), or more likely by leaching of $K_2O \cdot 6SiO_2$ from the potash feldspar, as demonstrated by the experiments of Morey cited previously.

At water pressures less than the total pressure, muscovite could form only in the solid state, since the muscovite breakdown curve lies at lower temperatures, and the minimum melting curve of granite lies at higher temperatures than those indicated for water pressures equal to the total pressure (cf. Yoder, 1955). The absence of muscovite phenocrysts in rhyolites is clearly indicated by the relations in Fig. 16.

The amount of muscovite in a granite appears to be limited. A measure of this limitation may be found in an examination of the normative corundum in

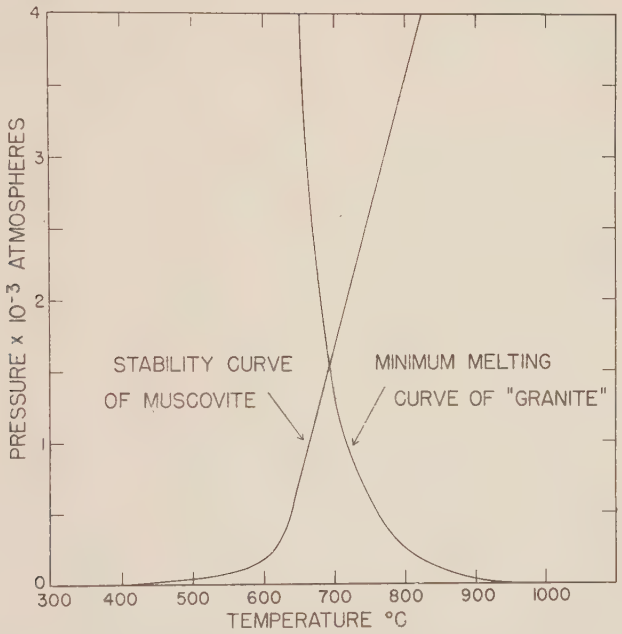


Fig. 16. Relationship of the breakdown curve of muscovite (Fig. 6) to the minimum melting curve of granite determined by Tuttle and Bowen (1953 p. 50).

granite analyses. This is a reasonable estimate, since neither biotite nor the common pyroxene contributes to normative corundum. The only conflict arises from some aluminous amphiboles, which as a group are not common in granites. In Fig. 17 is plotted the weight per cent of normative corundum of about 1640 analyzed rocks of granitic composition (Washington, 1917). About 37 per cent of the granitic rocks analyzed (granites, rhyolites, pegmatite, aplite, etc.) contain no normative corundum, and the average normative corundum of all such rocks is 1·23 per cent, which amounts to about 4·6 per cent muscovite. This average is not of great import, because of the J-shaped distribution. In addition, the error in the analyses of Al_2O_3 may be as high as ± 1 per cent (Fairbairn *et al.*, 1951), which is equivalent to about $\pm 3{\cdot}7$ per cent muscovite. Errors in the analysis of

Na_2O, K_2O, and CaO also affect the normative corundum. About 8·7 per cent of the analyzed granites have normative corundum exceeding that expected of the most muscovite-rich granite observed by Chayes. (It is not likely that such rocks would be called granite by most petrographers, particularly a rock containing 35 per cent muscovite.) The conclusion obtained from this crude analysis is that granites are closely restricted in muscovite content.

An understanding of the restricted muscovite content of granites may be found in the work of Schairer and Bowen (1955) on the K_2O—Al_2O_3—SiO_2 system. They found that the mullite liquidus surface rises very steeply from the potash feldspar—tridymite—mullite eutectic, as well as from the mullite—potash feldspar boundary

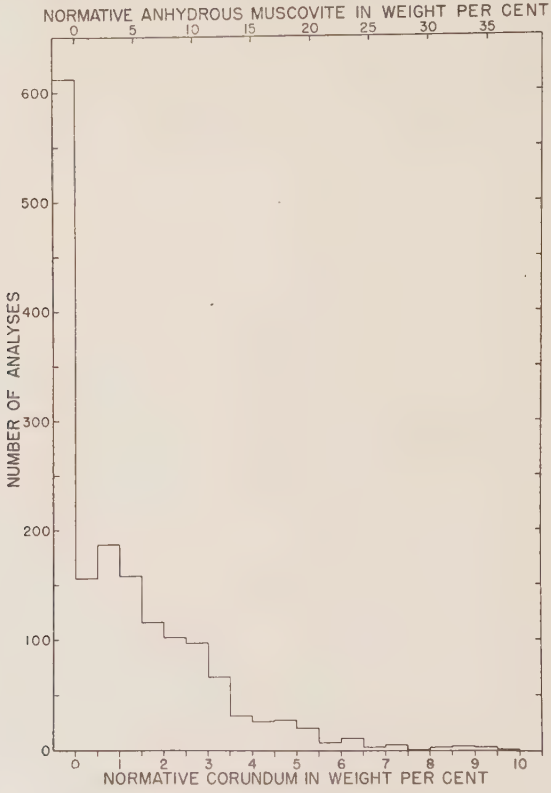


Fig. 17. Frequency of normative corundum in rocks of granitic composition based on about 1640 analyses compiled by Washington (1917).

curve (see Fig. 2). This feature is striking in more complex systems (Schairer, 1954, p. 531). For example, a 2 per cent increase of Al_2O_3 (7·5 per cent potential muscovite) from the eutectic composition raises the liquidus temperature 180°C! On the assumption that the eutectic composition is representative of granite and that the relative contour of the liquidus surfaces is maintained when water is added to the system, a small increase in normative corundum from which muscovite could be made produces a large rise in the liquidus temperature. This means that even the hottest magmas of granitic composition are not likely to

contain much alumina in excess of that required for the feldspars. The product of this argument is that granite magmas are restricted in Al_2O_3, and hence potential muscovite, by virtue of the steeply rising liquidus surface towards Al_2O_3. Of course, those granites formed by the metamorphism of sediments would not be restricted in their muscovite content. Granites very rich in muscovite are interpreted by some as having been formed by metasomatic processes.

The absence of muscovite in the one-feldspar granites may be accounted for, if the granite formed at a temperature above the solvus where the alkali feldspars form a complete series of solid solutions (Bowen and Tuttle, 1950). The upper stability limit of muscovite at 1000-bars water pressure is approximately at the maximum temperature of the solvus of the $NaAlSi_3O_8$—$KAlSi_3O_8$—H_2O system. Calcium raises the solvus to higher temperatures (Tuttle, 1952), so it is required that the one-feldspar granites in which muscovite is absent be poor in calcium. (A perusal of Washington's compilation of chemical analyses of igneous rocks indicates that those granites in which $K_2O \gg Na_2O + CaO$ are rich in muscovite.)

Corundum-bearing Alkaline Syenites

The experimental studies contribute to the knowledge of the temperature and pressure of formation of the corundum-bearing alkaline syenites. In such syenites corundum and potash feldspar crystals are observed to be contiguous and appear to be in equilibrium. These rocks usually contain biotite or hornblende, or both, establishing the presence of water during their formation. The assemblage potash feldspar + corundum + water can be in equilibrium only at conditions above the upper stability curve of muscovite. The maximum upper stability limit of muscovite, i.e., when the water pressure is equal to the total pressure, is given by Fig. 6. Below the stability curve of muscovite, potash feldspar + corundum + water would be expected to react to form muscovite. In experimental studies it has been found that corundum is exceptionally unreactive even in experiments of a year's duration, while potash feldspar (sanidine) reacts quickly, and is easily transported in the vapour. This relative behaviour appears to persist under natural conditions. In some corundum-bearing alkaline syenites, muscovite is found usually wholly within the corundum, either confined to the parting planes or randomly dispersed. In others it occurs as a peripheral alteration extending beyond the original faces of the corundum. In addition, some muscovite is found dispersed throughout the rock, but it is not possible to determine in all cases whether or not these books of mica had a core of corundum. It is concluded from these observations that the corundum-bearing syenites formed at pressures and temperatures above the stability curve of muscovite. On cooling, or during a subsequent reheating, potash feldspar (a) reacted with adjoining corundum, or (b) was transported in the vapour to corundum, and there reacted to form muscovite.

A unique rock has been described by Morozewicz (1899, p. 215), a corundum-orthoclase pegmatite, which must have formed in the presence of water at conditions above the breakdown of muscovite. In the absence of water, orthoclase and corundum are incompatible, according to the work of Schairer and Bowen (1955). On the basis of this occurrence, it seems reasonable to expect, in nature, dikes consisting mainly of muscovite.

Metamorphic Rocks

The muscovite breakdown curve fixes the *maximum* possible conditions of the second sillimanite or orthoclase isograd (Heald, 1950, p. 75). The reaction usually specified for this isograd is:

$$\text{Muscovite} + \text{quartz} = \text{orthoclase} + \text{sillimanite} + \text{water}.$$

The P-T curve of this reaction, when the total pressure equals the water pressure, would be expected to be at slightly lower temperatures than the P-T curve experimentally determined for the muscovite breakdown reaction. The preliminary experiments presented in a preceding section support this view.

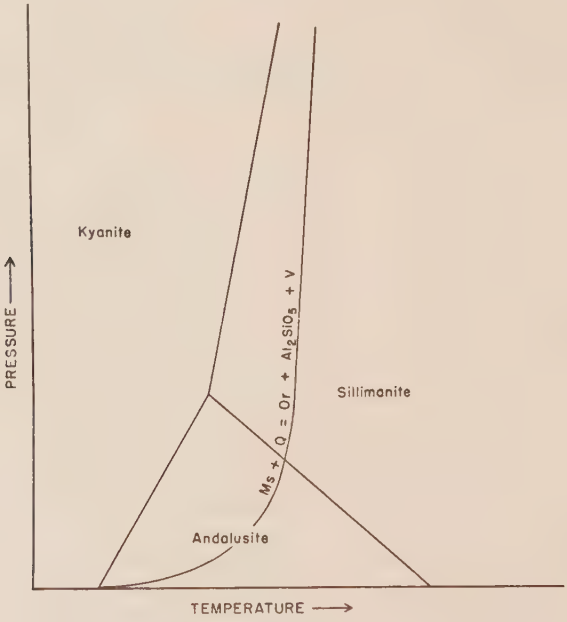


Fig. 18. Probable relationship of the Al_2SiO_5 polymorphs as suggested by Miyashiro (1949) and Thompson (1955) to the muscovite + quartz $\rightleftharpoons$ orthoclase + Al_2SiO_5 + water stability curve.

The polymorph of Al_2SiO_5 which results from this reaction is not clearly established for all conditions. Harker (1939, p. 56) has inferred from his field observations that the reaction yields andalusite. Ramberg (1952, p. 48) notes that sillimanite is the product when the pressure is high, and andalusite when the pressure is low. The relationship of the Al_2SiO_5 polymorphs as given by Miyashiro (1949) and Thompson (1955) to the above reaction is probably as in Fig. 18. These relations are in accord with the generalization made by Ramberg. Muscovite is also known to occur with all three polymorphs in the same rock (Hietanen, 1954, p. 331).

The appearance of a potash feldspar in a rock subjected to progressive metamorphism is not always the product of the above specified reaction. For example,

potash feldspar is a product of these proposed reactions involving muscovite (Turner and Verhoogen, 1951; Ramberg, 1952):

Muscovite + biotite + quartz = potash feldspar + cordierite + vapour

Muscovite + biotite + quartz = potash feldspar + hypersthene + cordierite + vapour

Muscovite + biotite = potash feldspar + garnet + vapour

Muscovite + sphene + quartz = potash feldspar + anorthite + rutile + vapour

Muscovite + calcite + quartz = potash feldspar + epidote + vapour

Muscovite + epidote = potash feldspar + anorthite + vapour.

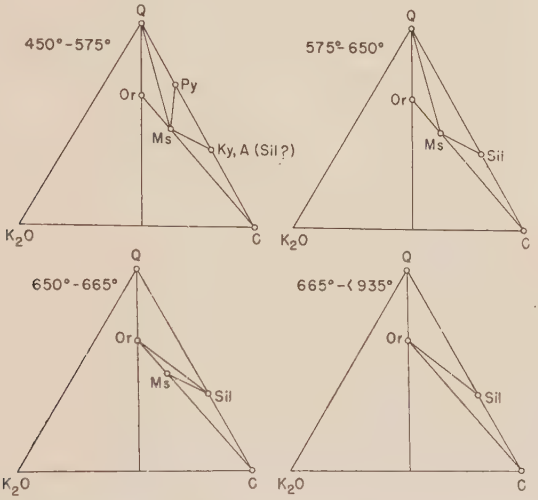


Fig. 19. Probable phase assemblages in a portion of the system K_2O—Al_2O_3—SiO_2—H_2O at 1000 bars water pressure. The pyrophyllite decomposition temperature is given by Roy and Osborn (1954).

It would be of interest to establish the presence of potash feldspar granules within muscovite in those rocks in which the muscovite is believed to be replaced by sillimanite needles. Chayes (1955) has demonstrated by modal analysis the appearance of potash feldspar as a by-product of the biotite-chlorite transformation.

On the assumption that the muscovite + quartz reaction yields potash feldspar, a polymorph of Al_2SiO_5 and vapour, the phase assemblages obtained in progressive metamorphism are as given in Fig. 19. The relationship of mullite to the phases indicated is not known in the presence of water.

The occurrence of abundant muscovite in the aureoles of some granites may now be examined. From the relations in Fig. 16 it is clear that muscovite will be preserved in the aureoles around granites having two feldspars and two micas (biotite and muscovite). The granite and metamorphic aureole of Dartmoor (Brammall and Harwood, 1932) show this relation. On the other hand, muscovite

is probably absent in the immediate contact zone surrounding the one-feldspar or one-mica granites having normative corundum.

Sediments

Three of the principal problems involving muscovite in sediments are the nature of the processes of its (1) destruction in weathering, (2) abrasion during transport, and (3) formation in diagenesis.

Destruction in weathering.—Muscovite was believed to be one of the most stable minerals in weathering. Thoulet (1913) listed muscovite among those minerals most indestructible in his "order of destruction." In Goldich's "mineral stability series" (1938, p. 56) muscovite is the most resistant of the aluminium silicates to decomposition. Pettijohn (1941) finds muscovite reported more commonly from older rocks than from younger ones, and on the basis of a "persistence index" rates muscovite as one of the most persistent. He thinks that the order of persistence based on the geologic record is related to solution effects following deposition. Muscovite is also exceptionally stable on the basis of a "weathering potential index" devised by Reiche (1945).

These estimates of stability of muscovite precede the acceptance and wide application of the term "illite." Grim (Trask, 1939, pp. 484, 487) states that illite "appears to be easily altered and is not apt to be a constituent of residual deposits" or the result of weathering processes. Most of the materials called illite were shown above to be a polymorph of muscovite, or mixed layers of muscovite and montmorillonite. Grim's view may be acceptable in view of the fine grain size of most materials called illite. The hydromicas present a possible example of the destruction of muscovite by weathering, and they may equally well be the direct weathering product of other minerals (e.g., feldspar). This process has been outlined in principal by many workers:

(1) feldspar → secondary muscovite → kaolinite; primary muscovite persists (Hickling, 1908)

(2) illite → hydrous mica-intermediates → montmorillonite → kaolinite → gibbsite (Jackson *et al.*, 1948)

(3) muscovite → Al-illite → Al-hydromica → montmorillonite (or beidellite) (Andreatta, 1949)

(4) illite → degraded illite → montmorillonite or kaolinite (Grim, Dietz, and Bradley, 1949).

C. S. Ross (personal communication, 1955) noted that the latter three processes imply that illite or Al-illite contains some magnesium in solid solution or in a mixed-layer mineral, or that magnesium-bearing solutions react with the intermediate products if montmorillonite is to be one of the final products. He is of the opinion that kaolinite is the more likely product of the weathering of muscovite or feldspar. Irrespective of the terminology, each of the processes outlined is intended to represent a continuous loss of K_2O and an increase of water and silica, and according to the work of Denison, Fry, and Gile (1929) the ratio of the loss of

K_2O to the gain in H_2O is 1 : 1 in relative weight per cent. There is no doubt that this chemical change does take place, but the question arises as to how this leaching process can take place continuously from a mica structure to a kaolinite or montmorillonite structure. An X-ray examination of the natural intermediate members of this process casts doubt on the continuity of the suggested processes.

Hickling (1908) was of the opinion that two distinct forms of muscovite existed in soils: primary muscovite from the parent rock and secondary muscovite from the alteration of feldspar. The primary muscovite persists (according to Hickling) throughout the soil profile, and secondary muscovite weathers to kaolinite. Ross and Kerr (1931, pp. 172–173) examined chemically materials like those described by Hickling as secondary mica, as well as those described as sericite by Stelle (1907), and concluded that they were not a mica, but similar to kaolinite in composition, but containing less water. An X-ray study of the materials studied by Ross and Kerr indicates that the "secondary muscovite" has a kaolinite structure. It appears in these cases that feldspar weathers directly to a kaolinite structure without an intermediate stage of mica.

Jackson *et al.* (1948) give examples of the various stages of weathering proposed. One example of "illite" was the Pennsylvanian underclays of Illinois, which the present writers found to contain two polymorphs of muscovite and montmorillonite. The "hydrous mica-intermediates" were represented by the Ordovician bentonites of Kentucky, which were found to be mixed-layer structures of muscovite and montmorillonite (see Brindley *et al.*, 1951, p. 158). It is believed, therefore, that the continuity of the process outlined by them cannot be demonstrated by their observations.

Andreatta (1949) deduced from a literature survey that his analyzed micaceous clay was a mixture of a member of a muscovite-montmorillonite series and a member of a biotite-montmorillonite series. He suggested that the X-ray patterns of the members within each series should be similar, because the mica and montmorillonite structures are similar. The present writers interpret the X-ray powder pattern published by Andreatta as that of a mixture of 2M-muscovite + pyrophyllite + kaolinite. The basal spacing of 9·52 Å is too small to be a normal muscovite or a mixed-layer structure. A dehydrated montmorillonite may have such a small basal spacing; however, Andreatta's analysis shows 7·71 per cent H_2O^+. The absence of the 002 reflection of the 2M muscovite and the presence of a very strong 006 may mean that the measurement of the 002 spacing is in error. These difficulties prohibit the use of this mineral as evidence of a member of a complete series from the micas to montmorillonite.

Grim, Dietz, and Bradley (1949) deduced their scheme from the observations that illite occurs abundantly in surficial material undergoing weathering. The weathering process results in the partial removal of potassium from between the unit layers of the mineral. The illite so "degraded" (see Hendricks, 1942, p. 285, who appears to have first used the term) is then carried to the sea, where it rapidly picks up potassium again, or it may undergo further weathering to kaolinite, montmorillonite, or other products. Grim, Dietz, and Bradley were unable to specify the exact nature of the "degraded illite," since it was only possible to study bulk sediment samples which consisted of illite, montmorillonite, kaolinite, and in some cases, chloritic material.

It is clear from this analysis of these weathering schemes that the continuity of the muscovite → montmorillonite (or kaolinite) weathering process has not been established. It seems evident that the process is more complex than the simple leaching of K_2O and the addition of water. In the plot of the composition of illites and montmorillonites given in Fig. 11 it is seen that changes in the M^{+2} group and silica content are required in addition to the substitution of H_3O^+ for K^+. The writers believe that a complete series between muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$, and aluminian montmorillonite, $(H_3O)Al_2(Si_3Al)O_{10}(OH)_2$, is structurally possible; however, the prevalence of mixed-layer structures casts doubt on the continuity of such a series. It is doubted that a continuous series between muscovite and kaolinite is tenable on structural grounds.

Abrasion in transport.—The grinding experiments by the writers and others indicate that muscovite is quickly reduced in size by abrasion. The efficiency of grinding in the laboratory, however, far exceeds that in nature. Russell (1937) showed that the mineral composition of the Mississippi River sands was changed only in a minor way after 1100 miles of transport. The micas were rare or absent in the sand samples taken, and Russell was of the opinion that most of the micas remained in suspension and were deposited in the silts. Van Andel (1950) also found that even the low-resistant minerals hornblende and augite suffered little loss by abrasion in 700 km of transport down the Rhine River. For these reasons it is unlikely that muscovite is destroyed by abrasion in transport, and detrital muscovite should therefore be commonly observed in marine sediments. Some of what is now called illite is probably detrital muscovite.

Authigenic growth.—Evidence of the growth of muscovite in sediments has been presented by many workers. Examples of the types of observation made are now reviewed. Grim, Dietz, and Bradley (1949, p. 1806) have observed that the illite content of the sediments off the coast of California increased seaward, and that the illite content increased with depth in the near-shore cores. This was interpreted to mean that potassium was taken up from the sea-water by the clay debris to form illite. Potassium was believed to be adsorbed by montmorillonite, but the major consumer was thought to be a degraded illite-weathering product. On the other hand, van Houten (1953) noted that the K_2O content of the alluvial soils of the Mississippi River drainage basin, and the delta alluvium, was similar to that of the Gulf of Mexico deposits. In support of the argument presented by Grim, Dietz, and Bradley, Volk (1933) found that soils treated with potash fertilizer fix potassium through the formation of a mica. In addition, Grimshaw (Griffiths, 1952) reports that he has treated illite hydrothermally, using potassium salts, and obtained a product approaching muscovite. There appears to be, then, a basis for concluding that mica can form by the simple alteration of some soil materials, and hence from materials deposited in the sea.

The authigenic illitic mica described by Norin (1953) is very similar in appearance to the vermicular mica-like materials illustrated by Ross and Kerr (1948), which were shown to be kaolinite. On the basis of Norin's X-ray data, the sediments of the Tyrrhenian Sea contain 1M-muscovite, 2M-muscovite, kaolinite, montmorillonite, quartz, and possibly a chlorite. It is not certain that

the delicate mica-like structures photographed by Norin are either a mica or a kaolinite, although there is little doubt that the crystals developed *in situ*.

The alleged growth of mica in sediments has apparently taken place at the expense of montmorillonite (Dietz, 1941) or kaolinite (Grim, Dietz, and Bradley, 1949). The proposed mechanisms may be written as follows:

(a) $3Al_2Si_4O_{10}(OH)_2 + 2K^+ \rightarrow 2KAl_2(Si_3Al)O_{10}(OH)_2 + 6SiO_2 + 2H^+$,

(b) $3Al_4Si_4O_{10}(OH)_8 + 4K^+ \rightarrow 4KAl_2(Si_3Al)O_{10}(OH)_2 + 6H_2O + 4H^+$.

Two important points are to be noted from this formulation. First, the growth of muscovite takes place in an "acid environment." In sea-water this effect is probably negligible. On the other hand, a low pH will cause the reaction to proceed in the reverse direction, and muscovite is attacked by some acids (Thiebaut, 1925; Pask and Davies, 1945). Secondly, in both proposed mechanisms a drastic reconstruction of the structure is involved. The change from montmorillonite to muscovite cannot be achieved simply by stuffing potassium between the layers. The shift of aluminium from an octahedral site to a tetrahedral site is required for the formation of muscovite from montmorillonite or kaolinite. In the high-silica micas such as glauconite, celadonite, and some sericites, this change is reduced considerably.

The mechanisms by which muscovite can grow by reaction in a sediment are greatly limited by the paucity of potassium-bearing minerals. In addition to the above-described alterations of clay minerals, potash feldspar and leucite are the only common potential sources of potassium. Although reactions of these two minerals with the aluminium silicate clays are possible, it is not likely that these take place under near-surface conditions. The reconstruction of montmorillonite and kaolinite remains the most probable mechanism by which muscovite grows in sediments.

In view of the reconstructive nature of these growth mechanisms, it is likely that growth will take place in the same manner observed in the laboratory. As shown in Fig. 10, growth in the laboratory took place first as a one-layer disorder crystal which subsequently ordered to a 1M muscovite. As demonstrated in previous sections, the 1M mica is common in nature.

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Hydrogen isotope fractionation between ice and water*

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Abstract—The equilibrium constant for the exchange of deuterium between ice and water is calculated from available thermodynamic data. At 0°C, ice is enriched in deuterium by 1·92 per cent compared to the water with which it is in equilibrium. The effect of dissolved salts is estimated to be only a lowering of the freezing-point. The application to some natural processes is considered.

The fractionation of hydrogen isotopes by the freezing of water or the melting of ice is a process of considerable geochemical interest. The experimental results obtained in the past (including some laboratory experiments) have varied greatly, even with respect to the direction of enrichment (Ingerson, 1953). In most of the earlier work, no attempt was made to calculate theoretical limits for the isotope effect. Eucken and Schäfer (1935) set up the necessary formulation for such a calculation, and applied the results to the specific case of isotopic enrichment in the residual ice of glaciers. The purpose of this paper is to obtain the equilibrium constant for hydrogen-isotope exchange during the freezing of water, using the best available thermodynamic data, and to consider the application to geologic processes.

Consider the equation for the freezing of pure water at equilibrium:

$$H_2O\ (\text{solid}) + HDO\ (\text{liquid}) = H_2O\ (\text{liquid}) + HDO\ (\text{solid}) \qquad (1)$$

with the equilibrium constant $K = [(HDO)/(H_2O)]_{solid}/[(HDO)/(H_2O)]_{liquid}$. At the natural abundance level of deuterium, $K = (D/H)_{solid}/(D/H)_{liquid}$. The value of K can be obtained under two assumptions:

(a) The rule of the geometric mean (Bigeleisen, 1955), which in this case states that $K = \sqrt{K'}$, where K' is the equilibrium constant for

$$H_2O\ (\text{solid}) + D_2O\ (\text{liquid}) = H_2O\ (\text{liquid}) + D_2O\ (\text{solid}) \qquad (2)$$

(b) H_2O and D_2O form ideal solid and liquid solutions. The validity of this is shown by the very small heat of mixing of the liquids, ~1–2 cal/mole (Eucken and Schäfer, 1935).

From thermodynamics, the following equation applies to the solid-liquid equilibrium between two-component systems forming ideal solutions in both phases:

$$\frac{d \ln [N_A\ (\text{liquid})/N_A\ (\text{solid})]}{dT} = L_A/RT^2 \qquad (3)$$

where N_A is the mole fraction of component A, L_A is the heat of fusion of pure A, and T is the absolute temperature (Rossini, 1950, p. 304). At temperatures near

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the freezing-point, $L_A = L_A^0 + (T - T_A)\Delta c_{P,A}$, in which $\Delta c_{P,A}$ is the difference in heat capacities between solid and liquid, and L_A^0 is the heat of fusion at the freezing-point, T_A. Equation (3) is integrated after the preceding expression for L_A has been substituted; the lower limit of integration is set at T_A, at which temperature $N_{A,l} = N_{A,s} = 1$. The result is

$$\ln (N_{A,l}/N_{A,s}) = \frac{L_A^0 - \Delta c_{P,A} T_A}{R}\left(\frac{1}{T_A} - \frac{1}{T}\right) + \frac{\Delta c_P}{R} \ln \frac{T}{T_A} \tag{4}$$

Applying this equation to both H_2O and D_2O, and combining the results, one obtains $\log K = (\log K')/2 =$

$$\frac{L^0_{H_2O} - \Delta c_{P,H_2O} T_{H_2O}}{4{\cdot}606R}\left(\frac{1}{T_{H_2O}} - \frac{1}{T}\right) - \frac{L^0_{D_2O} - \Delta c_{P,D_2O}\, T_{D_2O}}{4{\cdot}606R}\left(\frac{1}{T_{D_2O}} - \frac{1}{T}\right)$$
$$+ \frac{\Delta c_{P,H_2O}}{R} \log \frac{T}{T_{H_2O}} + \frac{\Delta c_{P,D_2O}}{R} \log \frac{T_{D_2O}}{T} \tag{5}$$

The pertinent numerical quantities are given by Kirshenbaum (1951), and the tables compiled by Rossini *et al.* (1952):

$L^0_{H_2O}$ = 1436·3 ± 1 cal/mole at 0·00°C = 273·16°K.
$L^0_{D_2O}$ = 1515 ± 10 cal/mole at 3·82°C
$\Delta c_{P,H_2O}$ = 8·911 entropy units at 0·00°C
$\Delta c_{P,D_2O}$ = 9·49 entropy units at 3·82°C

When these quantities are substituted in (5), the formula for K becomes

$$\log K = 0{\cdot}40948 - 0{\cdot}14568 \log T - 12{\cdot}643/T \tag{6}$$

At 0°C, $K = 1{\cdot}0192 \pm 0{\cdot}0002$; the principal source of error in the calculated value is the uncertainty in $L^0_{D_2O}$. The temperature variation in the last two terms very nearly cancels out near 0°; the change with temperature is approximately $d \log K/dT = -6 \times 10^{-5}$. At −2·0°C, $K = 1{\cdot}0195$. For a more accurate calculation of the change with temperature, one needs more data on the temperature dependence of Δc_P.

In the case where the water contains large amounts of dissolved salts, e.g., seawater, the appropriate equilibrium corresponding to (2) is

$$H_2O \text{ (solid)} + D_2O\text{(liquid, } m \text{ molal solute)} = D_2O\text{(solid)} + H_2O \text{ (liquid, } m \text{ molal solute)} \tag{7}$$

The equilibrium constant is $K'' = K' a_{D_2O}/a_{H_2O}$, where a is the activity of the solvent in the solution of m molal solute (Rossini, 1950, p. 321). The salinity of sea-water in arctic and antarctic regions where sea ice is formed is 34–35‰, which corresponds to approximately 0·6 molal sodium chloride as the chief constituent (Sverdrup *et al.*, 1946). The data needed to calculate the solvent activity of H_2O and D_2O in sodium chloride solutions are not available; however, data for potassium chloride solutions are (La Mer and Noonan, 1939). If the usual method of obtaining solvent activity from solute activity (Rossini, 1950, p. 330) is used,

the ratio of the activities of D_2O and H_2O in 0·6M KCl at 25°C is found to be unity, within experimental error. The activity of water is even closer to unity in sodium chloride solutions than in potassium chloride solutions of the same concentration, and the temperature effect on going from 25° to 0° is small. Hence, the activity effect on the equilibrium constant is negligible. The remaining effect, of course, is the lowering of the freezing-point due to the solute; this is about 1·8° at a salinity of 35‰. At this temperature, $K = 1{\cdot}0195$, from equation (6).

The equilibrium constant derived above gives the actual ratio of deuterium abundances in the two phases at equilibrium. If, after some fraction θ of phase-separation has occurred, the abundance is compared with the original abundance, a slightly different relation applies. Consider a process in which phase 1 is converted to phase 2, and θ = amount in phase 2/original amount in phase 1. There are two cases:

I. Throughout the separation process the entire phase 2 is in equilibrium with the entire phase 1. Then define

$$\alpha = (\mathrm{D/H})_2/(\mathrm{D/H})_1 = N_{\mathrm{D},2}/N_{\mathrm{D},1} \tag{8}$$

By material balance

$$N^0_{\mathrm{D},1}Q^0_1 = N_{\mathrm{D},2}Q_2 + N_{\mathrm{D},1}Q_1 \tag{9}$$

in which Q is the number of moles, N is the mole fraction, and the superscript 0 refers to the initial condition. Since $\theta = Q_2/Q^0_1$,

$$N^0_{\mathrm{D},1} = \theta N_{\mathrm{D},2} + (1 - \theta)N_{\mathrm{D},1} \tag{10}$$

$$N_{\mathrm{D},2}/N^0_{\mathrm{D},1} = \theta^{-1}[1 - (1 - \theta)N_{\mathrm{D},1}/N^0_{\mathrm{D},1}] \tag{11}$$

From (8) and (10),

$$N_{\mathrm{D},1}/N^0_{\mathrm{D},1} = [1 + (\alpha - 1)\theta]^{-1}$$

So that

$$\frac{N_{\mathrm{D},2}}{N^0_{\mathrm{D},1}} = \frac{(\mathrm{D/H})_2}{(\mathrm{D/H})^0_1} = \frac{\alpha}{1 + (\alpha - 1)\theta} \tag{12}$$

Equation (12) applies to the case when ice is frozen slowly from water under equilibrium conditions, and the ice particles are small enough so that there is equilibrium throughout the solid phase.

II. During the separation process, an infinitesimal amount of phase 2 is in equilibrium with the entire phase 1 at any instant, and phase 2 is being continually removed from the separation process. This situation is entirely analogous to a Rayleigh distillation; the appropriate equations are derived, for example, by Cohen (1951), and the derivation will not be repeated here.

The result is

$$(\alpha - 1)\ln(1 - \theta) = \ln\frac{N_{\mathrm{D},1}/(1 - \mathrm{N}_{\mathrm{D},1})}{N^0_{\mathrm{D},1}/(1 - N^0_{\mathrm{D},1})} + (\alpha - 1)\ln\left(\frac{1 - N^0_{\mathrm{D},1}}{1 - N_{\mathrm{D},1}}\right) \tag{13}$$

Since $1 - N^0_{\mathrm{D},1} \cong 1 - N_{\mathrm{D},1}$ and $\alpha \cong 1$, equation (13) may be expanded to

$$N_{\mathrm{D},1} - N^0_{\mathrm{D},1} = -N^0_{\mathrm{D},1}(1 - N^0_{\mathrm{D},1})(\alpha - 1)\ln\frac{1}{1 - \theta} \quad ,$$

which corresponds to equation (9), p. 152 of Cohen (1951). Within the error of calculating K, $1 - N^0_{D,1} = 1$, at the natural abundance level. Hence

$$N_{D,1}/N^0_{D,1} = (D/H)_1/(D/H)^0_1 = 1 + (\alpha - 1)\ln(1 - \theta) \qquad (14)$$

Since, from (10), $N_{D,2} - N^0_{D,1} = (\theta - 1/\theta)(N_{D,1} - N^0_{D,1})$, then

$$N_{D,2}/N^0_{D,1} = (D/H)_2/(D/H)^0_1 = 1 + (\alpha - 1)\left(\frac{\theta}{1-\theta}\right)\ln\frac{1}{1-\theta} \qquad (15)$$

If ice were frozen in a closed system in such a way that only an infinitesimal layer at the surface was in equilibrium with water, equations (14) and (15) would be applicable. This situation may be approximated during fairly rapid freezing, since the isotopic exchange equilibrium is certainly attained much more rapidly between the solid surface and the liquid than between the bulk solid and the liquid.

Eucken and Schäfer (1935) have derived equations similar to those of Case II, and have applied them to the deuterium enrichment in residual glacial ice. Rather large fractionations can occur; for example, when $\theta = 0{\cdot}999$, $(D/H)_{ice}/(D/H)^0_{ice} = 1{\cdot}128$. However, as they point out, the assumption that the bulk of glacial ice is in equilibrium with the melt water, which is continually running off, may not be valid.

It is difficult to assess, in general, what effect the deviation from equilibrium conditions in natural freezing (or melting) processes will have on the observed fractionation. For example, it is quite probable that freezing of sea ice does not occur under equilibrium conditions, and brine may be trapped in the ice as it forms (Sverdrup *et al.*, 1946). The latter fact would lower the observed fractionation. In general, however, a knowledge of the theoretical effect to be expected should be useful in forming hypotheses about the processes which occur.

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Sodium and potassium in meteorites

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Abstract—Using a method previously published, the sodium and potassium contents of nineteen chondritic meteorites, sixteen achondrites, and two carbonaceous chondrites, and the olivine from four pallasites, have been determined. The latest group of chondrites show the same total spread of values indicated in the previous publication. 90 per cent of all sodium values for chondrites lie between 0·60 and 0·76 per cent and potassium between 0·072 and 0·096 per cent. The olivine from pallasites is very uniform in alkali content with K 0·009–0·011 per cent and Na 0·04–0·05 per cent. The achondrites have quite variable sodium and potassium contents.

Introduction

Some time ago Urey and Edwards (1955) described an evaporative method for estimation of sodium and potassium in silicates, and gave results for certain meteorites, mainly chondrites and carbonaceous chondrites. At that time we had available to us only a few achondrites. Since then we have been able to obtain many more achondrites and other meteorites, the sodium and potassium analyses of which are reported here.

The measurements were made in exactly the same way as previously described.

Chondrites

We had previously shown on the basis of our analysis of twenty-one chondrites that this group contains an average of 0·67 per cent sodium and 0·085 per cent potassium with a total spread of values between 0·47 and 0·74 per cent and between 0·058 and 0·102 per cent respectively. The analysis of an additional nineteen chondrites confirms our original findings, the new results alone giving average sodium 0·66 per cent and potassium 0·081 per cent, with a total spread of values between 0·48 and 0·72 per cent and between 0·072 and 0·105 per cent respectively.

The latest results for chondrites are shown in Table 1.

The consistency of the two groups of results (previous publication and this paper) taken separately suggests that they each constitute a rather representative sample of all chondrites. It seems worth while, therefore, to make histograms of all the chondrite results to show the distribution of values, and these are shown in Figs. 1 and 2. The class interval for the histograms has been chosen as approximately 6 per cent, which is equal to the total variation in individual results (± 3 per cent). Intervals less than this would not be significant, as the experimental method does not take account of smaller changes in composition. From the histograms, it is clear that 90 per cent of all values fall between 0·60 and 0·76 per cent for sodium and between 0·072 and 0·096 per cent for potassium, which confirms the spread of values suggested in our previous publication (cf. Brown and Patterson, 1947).

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Table 1. Sodium and potassium in chondrites

Name	Na (per cent)	Average Na (per cent)	K (per cent)	Average K (per cent)	Ratio Na/K
Alfianello	0·72	0·72	0·092	0·092	7·8
Bath Furnace	0·66 0·66	0·66	0·072 0·071	0·072	9·3
Beardsley	0·65 0·65	0·65	0·106 0·104	0·105	6·2
Bluff	0·61 0·59	0·60	0·073 0·072	0·073	8·3
Bori	0·71	0·71	0·091	0·091	7·8
Framington	0·69 0·72	0·71	0·084 0·086	0·085	8·3
Homestead	0·70 0·73	0·72	0·089 0·091	0·090	7·9
Hugoton	0·48 0·48	0·48	0·079 0·079	0·079	6·1
Kesen	0·61	0·61	0·081	0·081	7·5
Lançon	0·61 0·61	0·61	0·082 0·081	0·082	7·5
Lissa	0·67	0·67	0·097	0·097	7·0
Modoc	0·69 0·68	0·69	0·088 0·090	0·089	7·7
Pantar	0·66 0·68	0·67	0·088 0·088	0·088	8·5
Potter	0·60	0·60	0·079	0·079	7·6
Queens Mercy	0·64	0·64	0·083	0·083	7·7
St. Michel	0·68	0·68	0·091	0·091	7·5
Tromøy	0·63	0·63	0·083	0·083	7·6
Walters (black)	0·72	0·72	0·089	0·089	8·1
Walters (grey)	0·70	0·70	0·091	0·091	7·7
Indarch	0·75	0·75	0·088	0·088	8·6
Paragould (original)	0·71 0·69	0·70	0·095 0·095	0·095	7·4
Paragould (heated) (see text)	0·62 0·61	0·62	0·104 0·105	0·105	5·9

Unfortunately, there are still not enough examples of meteorites in the Urey and Craig (1953) low group to be able to say whether the alkalis are different from those of their high group. Certainly the difference, if any, must be small, as the

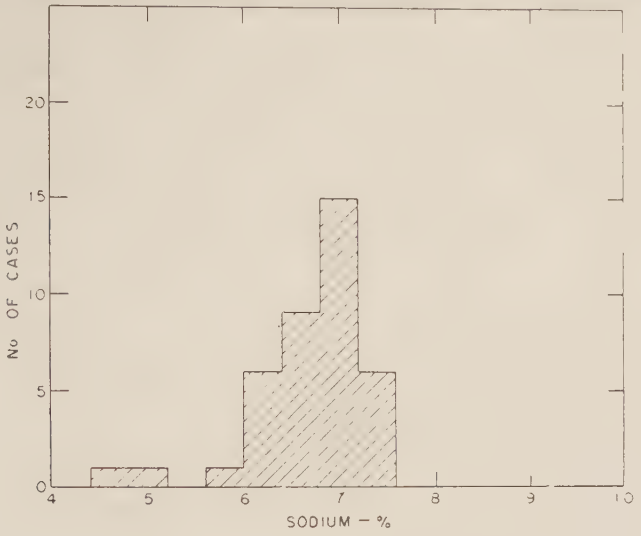

Fig. 1. Histogram of sodium in chondrites, total thirty-nine cases.

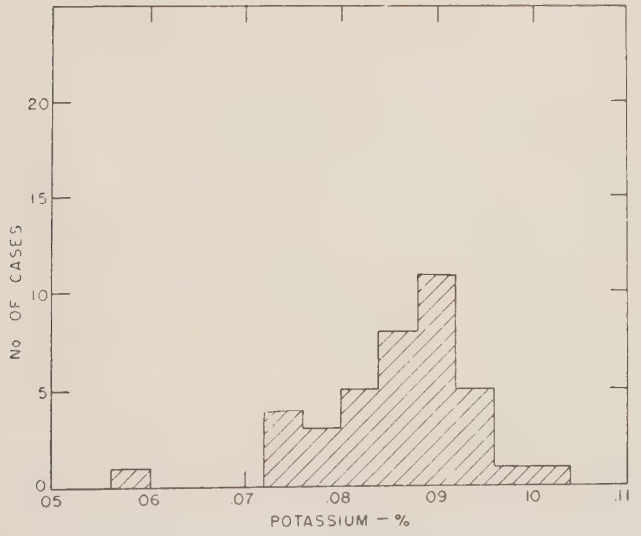

Fig. 2. Histogram of potassium in chondrites, total thirty-nine cases.

histograms do not show distinct twin peaks; but this might simply mean that the difference was of the same order as the experimental error, and would become detectable if a sufficient number of samples were examined. The existence of the groups suggested by Urey and Craig is now well established from recent analysis by Wiik (1955).

The latest result for Beardsley is interesting. The Beardsley previously analysed and reported in the earlier publication was a specimen from Nininger's collection (1950). The Beardsley meteorite is recorded in catalogues as a fall, but Nininger's specimens were recovered over a year after the original fall and were, therefore, exposed to ground-water for this period. In the previous publication, Urey and Edwards drew attention to this; and, because the stone had the highest concentration of potassium which we had then observed in a chondrite, there was doubt regarding whether the potassium had been increased in the period when the stone was exposed to the weather. In the interval, we obtained from Dr. E. W. Heinrich, of the University of Michigan at Ann Arbor, a fragment of Beardsley which was from the original collection recovered only a day or so after the recorded fall. This is the specimen the analysis of which is recorded here. Within the experimental error, it has the same potassium content as the Nininger specimen.

Our previous concern was that, if the potassium in Beardsley was not entirely meteoritic, the age by the argon-potassium measurements of Wasserburg and Hayden (1955) would have been somewhat low with respect to the true age. The present result removed completely any doubt which we previously held of the validity of Wasserburg and Hayden's result.

Through the courtesy of Dr. S. K. Roy of the Chicago Field Museum, samples from widely different parts of the world have been included in the present study of alkalis in chondrites.

Indarch, previously listed as a carbonaceous chondrite (Prior and Hey, 1953), is included here with chondrites on the basis of recent analysis by Wiik (1955). The sodium and potassium concentrations are clearly representative of ordinary chondrites.

There has always been some conjecture regarding the reason for different-coloured veins in certain stones. For this reason, veins in Walters were analysed separately to ascertain if there was a difference in alkalis; and the results for different parts of the same hand specimen are shown separately under "black" and "grey" in Table 1. (The two results were averaged and used as a single value in computing the main average for chondrites.)

If the veining were due to heating *in exposed conditions* where the alkalis would be free to vaporize, some difference might occur. No difference greater than the experimental variation is observed. It should be noted that coloured veins could occur due to differential heating under confined conditions with little or no change in alkali content.

An experiment was carried out on the Paragould meteorite (which exhibits light- and dark-coloured veining) to find whether alkali loss would readily occur on heating in an exposed condition. A small fragment (about 10 gm) was taken from a light-coloured vein in the meteorite. The sodium and potassium were measured, using half of the sample, and the remainder was heated three hours in vacuum at 950–1000°C, and the alkalis determined on this portion. The results shown at the end of Table 1 are inconclusive. The sodium is slightly reduced, as would be expected, but the potassium is inexplicably rather higher than in the original. There was no marked change in colour. More extensive experiments on the vaporization of alkalis are envisaged, and will be conducted when suitable specimens are available.

Achondrites

In the previous investigation, few specimens of achondrites were available; and in the interval other samples have been obtained, the analyses of which are shown in Table 2. As there were only four analyses of achondrites in the previous publication, they are included here for reference.

The analyses are listed in general under the classification of Prior and Hey (1953), but arranged so that they form the main groups suggested by Urey and Craig (1953). The latter authors place the achondrites on a chemical basis in two main groups – chondritic achondrites (achondrites with major chemical composition rather like chondrites) and basaltic achondrites (major chemical composition like basalts). The amphoterites are called amphoteric chondrites by Urey and Craig.

The achondrites are much more variable in sodium and potassium content than the chondrites. Two samples of Bishopville, *A* and *B* in the table, give distinctly different values. There is no difference in the appearence of the two samples, both from the Chicago Field Museum collection. Both Stannern specimens are from the same collection, and show some difference in the potassium concentration.

Jelica is a brecciated stone described by Prior and Hey (1953) as monomict. The dark- and light-coloured fragments from adjacent points in the specimen gave entirely different potassium contents, and indicate that the stone is a polymict breccia. Pasamonte is composed of dark and light breccia very like Jelica. The sodium and potassium in the two parts is only very slightly different, as the table shows.

In view of this kind of variation within single stones, a very large group of samples would have to be examined before critical conclusions regarding average composition of the various subgroups could be reached. On the basis of the major chemical compositions, Urey and Craig (1952) placed the aubrites (Bishopville, Shallowater, Bustee), the ureilite (Goalpara), and the diogenite (Johnstown) in the same class, and termed these chondritic achondrites. From the alkali analysis, there appears to be a distinct sub-group (or entirely separate group) with very low alkali content within this classification.

Although there is a wide variation of alkali content within the Urey and Craig group of basaltic achondrites (which includes eucrites, howardites, and the nakhlite) there is no indication of distinct subgroups, at least among the few analyses available at the moment.

The *average* alkali concentration of the three amphoterites is rather like that of the chondrites, and is corroborative of the classification of these by Urey and Craig as amphoteric chondrites.

Arcadia is classified by Prior and Hey only as an achondrite, and is listed at the end of Table 2 along with Cumberland Falls. Arcadia appears to be most closely related to the amphoterites in sodium and potassium content, but complete chemical analysis and mineralogical investigation would be necessary before a definite classification could be made. Cumberland Falls is a most interesting stone. It is described by Prior and Hey (1953) as "a breccia consisting of white aubrite and black enstatite chondrite" on the basis of an analysis by Shannon (1920).

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Table 2. Sodium and potassium in achondrites

Name and class (Prior and Hey)*	Na (per cent)	Average Na (per cent)	K (per cent)	Average K (per cent)	Average ratio Na/K	Class (Urey and Craig)†
Aubrites						
Bishopville A	1·04	1·00	0·085	0·083	12·0	CA
	0·96		0·081			
Bishopville B	1·17		0·122			
	1·17		0·122			
	1·15	1·16	0·122	0·123	9·5	CA
	1·15		0·124			
Shallowater	0·24	0·24	0·036	0·036	6·6	CA
Bustee	0·06	0·06	0·003	0·003	—	CA
Ureilite						
Goalpara	0·04	0·04	0·006	0·006	—	CA
Diogenites						
Johnstown	0·005	0·003	0·0010	0·0008	—	CA
	0·000		0·0005			
Eucrites						
Juvinas	0·31	0·33	0·038	0·038	8·7	BA
	0·34		0·037			
Stannern A	—	—	0·038	0·060	—	BA
Stannern B	0·43	0·43	0·069	0·069	6·2	BA
Nakhlite (*diopside-olivine achondrite*)						
Nakhla	0·44	0·44	0·102	0·102	4·3	BA
Howardites						
Frankfort	0·17		0·022			
	0·15	0·15	0·020	0·021	7·6	BA
	0·15		0·020			
Nuevo Laredo‡	0·41	0·41	0·047	0·047	8·7	—
Pasamonte (grey)	0·42	0·42	0·057	0·057	7·4	BA
Pasamonte (white)	0·38	0·38	0·052	0·052	7·4	BA
Pavlovka	0·13	0·13	0·017	0·017	7·4	BA
Petersburg	0·45	0·45	0·046	0·046	9·8	BA

Table 2—continued

Name and class (Prior and Hey)*	Na (per cent)	Average Na (per cent)	K (per cent)	Average K (per cent)	Average ratio Na/K	Class (Urey and Craig)†
Amphoterites						
Jelica (black)	0·69		0·060			
	0·71	0·70	0·057	0·059	11·9	AC
	0·70		0·059			
Jelica (grey)	0·67		0·143			
	0·67	0·67	0·140	0·141	4·8	AC
	0·67		0·140			
Manbhoom	0·69	0·69	0·086	0·086	7·9	AC
Vavilovka	0·70	0·70	0·095	0·095	7·3	AC
Not classified (*see text*)						
Arcadia	0·55	0·55	0·081	0·081	6·8	—
Cumberland Falls§	0·09	0·09	0·013	0·014	7·1	—
	0·10		0·014			

* Prior, G. T., and Hey, M. H. (1953) Catalogue of Meteorites (Brit. Mus. Nat. Hist.)

† Urey, H. C., and Craig, H. (1953) *Geochim. et Cosmochim. Acta*, **4**, 36.

Abbreviations: CA—Chondritic Achondrites
BA—Basaltic Achondrites
AC—Amphoteric Chondrites

‡ Nuevo Laredo. Specimen kindly provided by C. C. Patterson, California Institute of Technology, Pasadena, California. It is an unrecorded find of 500 gm referred to by Dr. Patterson in *Geochim. et Cosmochim. Acta*, **7**, 151, (1955), as a howardite, with a few chondrules.

§ Cumberland Falls is listed by Prior and Hey as aubrite and black enstatite chondrite. See text.

A large fragment (about 2·5 kg) was kindly provided for cutting by Dr. S. K. Roy of the Chicago Field Museum, so that a fresh surface exhibiting the black and white portions described by Prior and Hey might be exposed and sampled. The exposed face, though not uniformly white, showed only very fine black veins and small areas of darker grey. It was *not* possible to obtain a representative specimen of the dark material, and a fragment, judged to be as representative as possible of the whole meteorite, was ground up for analysis. From the low potassium and sodium contents, it seems clear that material of chondritic composition is only a minor fraction of the whole, and the analysis has for the time being been placed with unclassified achondrites.

Pallasites

Olivine from four pallasites was examined, and the results are shown in Table 3 along with those for an olivine bomb. The olivine bomb is from San Bernadino, California. The bomb was composed of an aggregate of small green fragments of olivine mixed with grains of dark material, probably pyroxene. As will be seen from the table, the sample was run compositely and separately.

The olivine portion of the bomb is quite similar to that from the pallasites, as would be expected. The olivines from the pallasites are much lower in sodium and potassium content than the chondrites, as would be expected of a silicate which was almost certainly differentiated at some depth within the parent asteroid or

Table 3. Sodium and potassium in pallasites and olivine bomb

Name	Na (per cent)	Average Na (per cent)	K (per cent)	Average K (per cent)	Average ratio Na/K
Pallasites					
Olivine from:					
Admire	0·05	0·05	0·009	0·009	5·5
	0·05		0·009		
Brenham	0·05	0·05	0·009	0·009	5·5
	0·05		0·009		
Finmarken	0·05	0·05	0·009	0·009	5·2
	0·04		0·010		
Mt. Vernon	0·04	0·04	0·011	0·011	3·9
	0·04		0·010		
Olivine Bomb					
Olivine Bomb (whole specimen)	0·22	0·22	0·018	0·017	12·9
	0·22		0·017		
Olivine Bomb (dark portion)	0·26	0·26	0·017	0·0173	15·3
Olivine Bomb (olivine portion)	0·07	0·07	0·011	0·011	6·3

asteroids. The fact that the alkalis of meteoritic olivine are higher than those found in dunites and other ultramafic rocks on the earth (Holyk and Ahrens, 1953) indicates somewhat less differentiation than in the ultramafic rocks.

The olivines from pallasites are remarkably constant in composition, as the table shows. The result for the Brenham Township meteorites is of special interest, in view of a recent publication referring to this meteorite by Thomson and Mayne (1955). On the grounds of their measurements and those of Dalton and Raesbeck (1954), these authors conclude that the stone and iron are of strikingly different ages. Thomson and Mayne find an age for the stone of $3{\cdot}5 \times 10^9$ years (using a K^{40}–A^{40} branching ratio of 0·125), while an age of $2{\cdot}8 \times 10^8$ years was deduced for the metal phase by the other authors.

Thomson and Mayne found the potassium in Brenham Township olivine to be 0·019 per cent, almost exactly double that found in the present investigation. If the potassium in the Brenham Township olivine is taken as 0·009, and Wasserburg

and Hayden's (1955) branching ratio is used, the age of the stone phase becomes about $4{\cdot}5 \times 10^9$ years. This would give almost exact agreement with the ages by the lead-lead method for three other stones according to Patterson (1955). It does not, however, give rise to any better agreement between the age of the metal and stony phases.

Table 4. Sodium and potassium in carbonaceous chondrites, water- and carbon-free basis

Name	Wiik's Group No.	Average	
		Na (per cent)	K (per cent)
Ivuna	I	0·73	0·075
Orgueil		0·72	0·073
Haripura	II	0·63	0·073
Mighei		0·56	0·053
Bokkeveld		0·54	0·052
Ornans		0·45	0·041
Felix	III	0·44	0·042
Warrenton		0·43	0·043
Mokoia		0·39	0·038
Murray	II	0·19	0·038

Recently, Reed and Turkevich (1955) have developed a neutron irradiation method for estimating uranium, and have shown that iron meteorites contain only about one-tenth of the uranium found by Dalton and Raesbeck. The ages found by the latter authors on the basis of helium-uranium measurements would, accordingly, be very much too low.

It seems most unlikely that the iron and stone so closely associated should exhibit different ages.

Carbonaceous Chondrites

Since the previous publication, it has been found possible only to obtain two other carbonaceous chondrites, Ornans and Warrenton.

A special effort was made to obtain these particular specimens, because they are representative of the low-volatile type of which our only specimens previously were Felix and Mokoia.

The results are shown in Table 4, together with averages of the previously published results, all on a total water- and carbon-free basis and arranged in order of decreasing sodium content. The table also shows subgroups proposed by Wiik (1955) on the basis of the total volatile and major constituent analyses. Apart from Murray, which we previously found exhibits abnormally low alkali content with reference to all the other carbonaceous chondrites, the order of decreasing sodium contents is in accordance with Wiik's proposed groups.

Acknowledgements—By some error, acknowledgements of assistance in the previous publication (Edwards and Urey 1955) were omitted in the final copy. This was unintentional, and I should now like to thank Drs. S. K. Roy and R. Wyant of the Chicago Natural History Museum for providing many specimens of meteorites. Dr. E. P. Henderson (U.S. National Museum, Washington), Dr. Clifford Frondel (Harvard Mineralogical Museum), Dr. J. Orcel (Museum Natural History, Paris), and Dr. Brian Mason (American Museum of Natural History) have all very kindly provided specimens. The specimen of Homestead meteorite was provided by Dr. W. H. Pinson (Massachusetts Institute of Technology), and that of Nuevo Laredo by Dr. C. C. Patterson (California Institute of Technology). I am especially indebted to Mrs. Jeanne Ingersoll, who has been responsible for a great deal of the experimental work reported in both papers. I am grateful to Dr. R. Landau (University of Chicago), who made available the spectrophotometric facilities used throughout the work.

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The Sr and Rb contents of the granite G-1 and the diabase W-1*

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(*Received* 1 *October* 1955)

Abstract—The interlaboratory calibration granite and diabase standards G-1 and W-1 have been analysed for Rb and Sr mass spectrometrically by the stable isotope dilution method. G-1 was found to contain 216 p.p.m. Rb and 233 p.p.m. Sr, and W-1 to contain 28·5 p.p.m. Rb and 177 p.p.m. Sr. These results are compared to other published analyses for these elements. If these new analyses are accurate, several published works, in which G-1 and W-1 were used as standards for Rb and Sr, are in need of revision.*

The Westerly, Rhode Island, granite, G-1, and the Centerville, Virginia, diabase, W-1, are interlaboratory calibration standards that have been extensively used to compare precision and accuracy of silicate rock analyses (Fairbairn *et al.*, 1951).

Isotope dilution analyses for Rb and Sr in G-1 and W-1 have recently been made by the writers, assisted by several students at M.I.T. These students performed five of the reported analyses, under our direction, in a laboratory course in geochemistry. The student analysts are: D. Benson, A. Brownlow, D. Eckhardt, R. Maehl, C. Prewitt, N. Short, G. F. Smith, and K. Stewart.

Table 1 gives the results of these isotope dilution analyses and compares them with values obtained by spectrochemical, chemical, and flame photometric techniques.

The earlier spectrochemical analyses are discussed by Fairbairn *et al.* (1951), and Ahrens (1954). The analysis for Rb by Horstman (Rock Analysis Laboratory, University of Minnesota) was communicated to the writers in a letter from S. S. Goldich. The spectrochemical results listed for Turekian (1955) are those given by him at the 1955 Washington meeting of the American Geophysical Union. His spectrochemical results for Sr in G-1 and W-1 were calibrated with a Lamont Laboratory, Columbia University, standard rock whose Sr content was checked by isotope dilution analyses. Isotope dilution analyses of G-1 and W-1 for Sr were not made.

The Sr values by Mitchell were later found by the analyst to be systematically high. For this reason we have not included them in the averages.

The Rb and Sr isotope dilution analyses reported in Table 1 are believed to have an absolute error of less than ± 5 per cent. This statement of accuracy is based on a comparison of results of analyses of identical samples by the writers, using the isotope dilution method, and analysts at other laboratories, using, in particular, isotope dilution, but also flame photometry, optical spectrometry, and conventional chemical techniques in some cases (Herzog *et al.*, 1955, and Herzog, in press.)

For relatively high (greater than 50 p.p.m.) concentrations of Rb and Sr, the precision of an individual routine isotope dilution analysis in our laboratory,

* *Editorial comment.* The Rb values given here agree very closely with those reported by Smales in a Letter in this Volume (p. 300).

expressed as per cent standard deviation, is better than $\pm 0{\cdot}8$ per cent, and replicate analyses of the same sample have a range of less than 2 per cent for Rb and less than 3 per cent for Sr.

The techniques and controls used in this work have been discussed in detail in connection with other work (Herzog *et al.*, 1954, 1955). In summary:

Three one-gram samples of G-1 and two samples of W-1 (1·00 and 2·00 grams) were weighed out carefully from the standard sample powders by conventional techniques. The weighed samples were placed in Pt dishes and decomposed with hydrofluoric and perchloric acids. Known amounts of Rb and Sr stable isotope "spikes" (Rb and Sr in which the isotope ratios had been highly modified relative to those occurring in nature) were added to each sample at the same time as the HF, and equilibrated with sample Rb and Sr during sample decomposition. (This "isotope dilution" method of analysis is discussed by Tilton (1954), among others.) After HF removal of silica, the perchlorate residues were dissolved in HCl. Rb and Sr were

Table 1. Strontium and rubidium content of diabase, W-1, and granite, G-1
(All values are parts per million by weight)

Analyst	Method	W-1		G-1	
		Sr	Rb	Sr	Rb
Herzog, Pinson, *et al.* (this paper)	Stable isotope dilution (mass spectrometer)	182 172	27·9 29·1	230 233 236	218 215
Ahrens, L. H., *et al.*	Optical spectrograph	250	64	250	550
Mitchell, R. L.	Optical spectrograph	420	15	900	590
Nockolds, S. R.	Optical spectrograph	180	20	280	250
Murata, K. J.	Optical spectrograph	120		120	
Harvey, C. O.	Optical spectrograph	180		220	
Turekian, K. K.	Optical spectrograph	110		265	
Sr average (all spectrochemical results except Mitchell)		168		227	
Rb average (all spectrochemical results)			33		463
Hey, M. H.	Chemical	450		450	
Horstman, E.	Flame photometer				205

separated from the remaining solution by ion exchange chemistry (Herzog *et al.*, 1954; Aldrich *et al.*, 1953; and Nachod, 1949), Sr was precipitated as the oxalate, and washed free of slight traces of Rb with H_2O. All manipulations were done in Pt, "Vycor" glass (which is extremely low in alkali and alkaline earth element content), or polyethylene. H_2O was purified by ion exchange followed by distillation in Vycor; ion exchange columns were also of Vycor. Purity of reagents was insured by optical spectrographic analysis of the residues obtained by evaporating volumes of reagent large compared with those used in a single analysis. During chemical processing, one Rb sample was inadvertently lost.

Rb and Sr concentrates were analysed for isotopic composition in individual mass spectrometric runs. Samples were placed on Ta ribbon filaments by capillary "Pyrex" droppers which had been cleaned and then "pre-contaminated" with the solutions to be analysed. The droppers were not re-used. The Ta filaments were proven to be uncontaminated by the element to be analysed by testing in the mass spectrometer prior to use. A 6-in. radius, 60°-field mass spectrometer was used for isotopic analysis. Ions were produced for analysis by thermal emission from RbCl and SrO (from the decomposition on the filament of $SrC_2O_4 \cdot H_2O$ on Ta filaments. The filaments were preoxidized in air for Sr runs to increase ion emission. Isotopic ion currents collected were amplified by an inverse-feedback d.c. amplifier with a voltage gain of 1. "Spiking" with the stable isotope tracers was so arranged that all peaks could be conveniently recorded for measurement at the same attenuation setting, on the 11-in. record of a strip chart recorder. The mass spectrum under investigation was swept repeatedly in alternate directions by varying magnet current while maintaining a constant ion acceleration voltage of about 2000 volts. Voltage scanning was not used, because it introduces serious mass discrimination effects. No correction factor has been applied to the results for mass spectrometer mass discrimination, which is believed to be less than 0·2 per cent per mass in the Sr, Rb region. At least fifty peak sets were measured for each of the determinations reported. The emission-weighted peak ratio average for the total sample was used to compute the sample-to-spike ratio for each analysis; this average was used to minimize errors due to systematic isotope fractionation during analysis.

The "spike" solutions used have been calibrated against standard, normal-isotope-composition Sr and Rb solutions carefully prepared by weighing and volumetric dilution (Herzog, Pinson and Cormier, 1955). Contamination for the total sample-processing procedure used was checked by tracer runs using pure Rb and Sr spike solutions. No contamination was found, but for the amounts of tracer used, the mass spectrometric isotope ratio measurement uncertainty of about $\pm 0{\cdot}5$ per cent results in the following contamination limits: Sr, less than 0·5 μgm, and Rb, less than 0·1 μgm, for the total processing of a one-gram rock sample.

If it is accepted that the M.I.T. isotope dilution analyses reported in Table 1 are more nearly accurate than the other analyses there reported, much previous analytical work in which G-1 and W-1 were used as Rb and Sr standards must be revised. Such analyses as those of Ahrens, Pinson, and Kearns (1952), Pinson, Ahrens, and Franck (1953), and Fairbairn *et al.* (1953) have been used by several investigators for estimating meteoritic, "cosmic," terrestrial, crustal, and igneous rock average Rb and Sr content. These derived values should also be revised. In particular, Ahrens's estimates of average igneous rock Rb and Sr content (350 and 220 p.p.m., respectively), given in Pinson, Ahrens, and Franck (1953) should be revised according to the data given in Table 2 below. Ahrens and his co-workers at the Cabot Spectrographic Laboratory used G-1 and W-1 as standard rocks. Elemental abundances in other samples were determined relative to these standards by densitometer comparison of intensity of the same atomic spectral line in sample and standard. The Rb and Sr concentrations reported for many samples were thus directly dependent upon the values assumed correct for W-1 and G-1, which are the values quoted in Table 2. These values were chosen by Ahrens after a comparison of the results of spectrographic analysis of W-1 and G-1 at several laboratories (Ahrens, 1954). Although the present work indicates that these Sr and Rb values for the standards were in error, there is a strong probability that the relative values found by the Cabot Laboratory workers are correct, to the stated limits of precision. The Sr and Rb concentrations found in the isotope dilution analyses reported in this paper can be used to recompute these published analyses. The necessary correction factors for each element in each standard are given in Table 2.

Table 2. Recalibration of Cabot Spectrographic Laboratory standard rocks for Sr and Rb concentration (parts per million by weight)

Analyst	W-1			G-1		
	Sr	Rb	Sr/Rb	Sr	Rb	Sr/Rb
Cabot Laboratory†	290	64	4·5	280	570	0·49
Present work	177	28·5	6·2	233	216	1·08
Correction factor	0·61	0·45	1·4	0·83	0·38	2·2

† Ahrens *et al.* (1952); Pinson *et al.* (1953); Fairbairn *et al.* (1953).

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* *Note regarding listing of unclassified A.E.C. documents as references.*

In this article, we have referred readers interested in details of analytical technique to the Annual Reports of this group to the Atomic Energy Commission (Unclassified U.S. A.E.C. Documents NYO 3934-II and 3935-II). These reports contain articles describing in detail methods and techniques of analysis used at this laboratory, including contamination control, reagent purification, and calibration of "spike" solutions. Many such details, while essential to a critical evaluation of the work, are considered by the writers to be of too little general interest to warrant publication in the severely burdened general periodical literature. These documents, which had a limited initial distribution, can be obtained upon request from the Director of the Nuclear Geophysics Section, Department of Geology and Geophysics, Mass. Institute of Technology, or to the publications office of the Atomic Energy Commission.

LETTERS TO THE EDITORS

Analytical error as a possible cause of the $t(\frac{206}{238}) > t(\frac{207}{235}) > t(\frac{207}{206})$ age distribution

(*Received* 26 *September* 1955)

It has been known for some time that the lead age distribution $t(\frac{207}{206}) > t(\frac{207}{235}) > t(\frac{206}{238})$ is present in a high proportion of U-bearing minerals. (See Fig. 1 of Ahrens, 1955a). Lead deficiency appears to be a likely cause (Ahrens, 1955a and b; Eckelmann and Kulp, 1955). Such apparent deficiency might be due to loss of lead itself or perhaps some unforeseen process. In a few specimens, the distribution $t(\frac{206}{238}) > t(\frac{207}{235}) > t(\frac{207}{206})$ has been observed, and this is presumably due to uranium deficiency. Such deficiency could, of course, arise from removal of uranium itself, the cause usually suggested (Holmes and Smales, 1948; Rankama, 1954 (p. 384); Louw, 1955, for example); but analytical error—serious underestimation of uranium—is another possibility, and will be considered briefly here.

We may note particularly that the minority distribution $t(\frac{206}{238}) > t(\frac{207}{235}) > t(\frac{207}{206})$ is common in those minerals where gravimetric procedures have been used to determine uranium when present at a low concentration; for example, monazite from Huron Claim, south-eastern Manitoba, and Las Vegas, New Mexico, and thucholite from Marievale and Blijvooruitzicht, South Africa, have this distribution. (See Holmes and Smales (1948) for analytical data on monazites in general, and Louw (1955) for the thucholites.) The reproducibility of gravimetric procedures in general frequently deteriorates quite sharply with decrease of concentration of an element (see, for example, Ahrens, 1954, Figs. 1 and 2); and Smales (in Holmes and Smales, 1948) has referred specifically to the inaccuracy of the gravimetric determination of low concentrations of uranium as in monazite, for example, where concentrations of 0·01–0·1 per cent U are not uncommon. Such inaccuracy is presumably due in part to incomplete precipitation; in fact, uranium is sometimes missed completely, as in monazite from Mt. Isa, Queensland, and Portland, Connecticut (see Holmes and Smales (1948) as general reference), where uranium is reported as 0·00 per cent. These monazites may, of course, contain extremely low uranium concentrations, but not zero.

If apparent uranium deficiency is due to serious underestimation of uranium, then one *principal* process only, namely, that which has brought about apparent lead deficiency, has been active in varying degree in the vast majority of uranium-bearing specimens. This might hold for thorium—lead ages as well; but as the thorium age-data, particularly those involving earlier observations, are often unsatisfactory, they have been omitted from the general discussion.

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Some trace-element determinations in G1 and W1 by neutron activation*

(*Received* 26 *September* 1955)

Ahrens and Fairbairn *et al.* have discussed separately the use of two rocks, a granite from Westerly, Rhode Island, U.S.A. (G1) and a diabase from Centerville, Virginia, U.S.A. (W1), as standards for the determination of both major and minor constituents of igneous rocks. After a large amount of work on a worldwide basis, which showed up a number of discrepancies in results and methods, the composition of these two rocks, so far as their major constituents are concerned, is fairly well agreed. On the other hand, there is still a good deal of disagreement about the minor-element content. The majority of results on the latter have been obtained spectrographically, although a few chemical determinations have been made, mainly using absorptiometric methods, in some cases rather near their detection limit. Polarographic determinations have also recently (Smythe and Gatehouse, 1955) become available for Cu, Ni, Co, Zn, and Cd.

In view of the fact that a good deal of work on the spectrographic determination of trace elements is under way in various centres at the present time, and some of this work may involve the use of G1 and W1 as standards, it seems desirable to give values obtained in this laboratory for some minor elements in these samples by an alternative chemical method, that of neutron activation. This method has been adequately described previously, but its advantages for this type of analysis may be restated as (1) high sensitivity, (2) freedom from reagent "blanks," (3) specificity (the identity of the radionuclide used in the determination can be confirmed by decay and energy measurements in addition to the chemical separations), (4) the avoidance of chemical operations with microgram or smaller quantities by using "carriers." The method, as usually employed, is a comparative one, but the standards used for comparison can normally be the pure element or a suitable compound.

In stating these advantages, it is not to be implied that the results quoted below are considered to be absolute values—they are given in the hope that they will be considered with the values obtained by other methods, so that eventually it might be possible to have an accepted list for G1 and W1. It is hoped to extend the list of elements determined as time permits.

	Au	Co	Cu	Ni	Pd	Rb
G1	0·010	2·1	8·7, 11·1,	1·0	< 0·01	221 p.p.m.
	0·009	2·1	8·8, 9·1,	1·0		254
			9·5, 9·6			243
W1	0·017	54, 52,	111·5, 111,	76, 71,	0·020	27 p.p.m.
	0·019	45, 46,	111, 108,	78, 73,	0·017	29
	0·016	50, 46	113, 119,	78, 63		26
	0·019		110, 109			

The various elements were determined by several people in collaboration with the author as follows: Au and Pd by E. A. Vincent (Dept. of Geology and Mineralogy, Oxford); Co, Cu, and Ni by D. Mapper and A. J. Wood; Rb by M. J. Cabell. Full details of the methods will be submitted for publication later.

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* *Editorial comment.* The Rb values given here agree very closely with those reported by Herzog and Pinson in a paper in this volume (p. 295).

INFORMATION FOR CONTRIBUTORS

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AHRENS, L. H. (1952) *Geochim. et Cosmochim. Acta* **2**, 168.

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EXTRACTS FROM EDITORS' PREFACE TO VOLUME ONE

It is in those branches of natural science which border older established disciplines that the need for critical survey reviews of progress has become greatest. This has arisen partly because subjects such as geochemistry and geophysics fringe and overlap so many other fields and partly because they are at present vigorous growing points in science. A principal aim of the annual series, Chemistry and Physics of the Earth, will be to provide authoritative and up-to-date surveys of progress for those actively engaged in geophysics and geochemistry. But it is hoped also that much of what is written will encourage the interest of the chemist and physicist in a study of our planet, not merely for its own sake, but because such a study often turns out to be of benefit to physics and chemistry. Another aim is to acquaint the geologist with the results and methods of geophysics and geochemistry, particularly as progress in earth science has been hindered by some lack of liaison between different groups. An attempt will be made to provide a balanced variety of topics with roughly equal emphasis on chemistry and physics, but certain topics will be considered fairly regularly.

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